Rearrangement of *O,S*-Dialkyl Dithiocarbonates to *S,S*-Dialkyl Dithiocarbonates Catalyzed by Tricaprylmethylammonium Chloride

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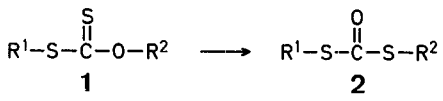
Symmetrical *S,S*-dialkyl dithiocarbonates **2** are usually prepared by reaction of thiols with phosgene[1]. Alternative routes involve thermal, acid-, or base-catalyzed rearrangements of *O,S*-dialkyl dithiocarbonates **1** to *S,S*-dialkyl dithiocarbonates **2**[2,3]. These rearrangement reactions have acquired a special interest, since *O,S*-dialkyl dithiocarbonates **1** can be easily prepared by a recent procedure under phase-transfer-catalysis conditions[4].

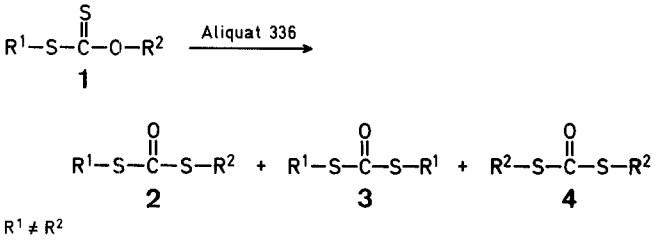


$R^1 = R^2$

Recently, we have shown that symmetrical *S,S*-dialkyl dithiocarbonates **2** can be obtained from *O*-methyl *S*-alkyl dithiocarbonates by two-phase reactions in the presence of a quaternary ammonium salt as phase transfer catalyst[2]. However, these conditions proved inadequate in the cases in which the *O*-alkyl group was not methyl and when both alkyl groups were methyl because side reactions (hydrolysis and subsequent reactions in the main) were in competition with the rearrangement to *S,S*-dialkyl dithiocarbonates.

For example, when *O,S*-dioctyl dithiocarbonate is heated at reflux under the reaction conditions indicated in Ref.[2], its disappearance is noted after 3 days and the main products are: octyl mercaptan, dioctyl sulfide, and dioctyl disulfide. Under the same conditions, *O,S*-dimethyl dithiocarbonate affords mainly unidentified low boiling products and only a small amount of *S,S*-dimethyl dithiocarbonate.

We have found, instead, that this rearrangement can be easily achieved by heating *O,S*-dialkyl dithiocarbonates **1** in the presence of tricaprylmethylammonium chloride at moderate temperatures (up to 100 °C) and for short times (90 min). Under these mild conditions, the yields (Table 1) are the same as or better than those obtainable using other methods reported.



$R^1 \neq R^2$

The new procedure offers an additional advantage in that both the preparation of *O,S*-dialkyl dithiocarbonates **1** and their rearrangement to *S,S*-dialkyl dithiocarbonates **2** are catalyzed by the same ammonium salt (Aliquat 336), so that the two reactions can be consecutively performed without the intermediary isolation and purification of **1**. Moreover, this reaction sequence seems especially promising for large scale preparations.

However, the present procedure is not suitable for preparing unsymmetrical *S,S*-dialkyl dithiocarbonates **2** ($R^1 \neq R^2$), since rearrangements of *O,S*-dialkyl dithiocarbonates containing different alkyl groups **1** ($R^1 \neq R^2$) give mixtures of **2** ($R^1 \neq R^2$) and the symmetrical *S,S*-dialkyl dithiocarbonates **3** and **4**. In these cases, the rearrangement **1**→**2** is apparently followed by transesterifications to **3** and **4**, also catalyzed by the ammonium salt.

S,S-Dialkyl dithiocarbonates **2** were identified by comparison of their b.p., m.p., retention times in G.L.C., and ^{1}H-N.M.R. spectra with those of authentic samples (Table 1). By-products were identified by G.L.C. (coinjection with authentic samples) and, when their isolation was possible, the assigned structures were confirmed by their ^{1}H-N.M.R. spectra.

Potassium *O*-Alkyl Dithiocarbonates:
Prepared by the standard procedure[8] from potassium hydroxide, excess of the required alcohol, and then carbon disulfide.

***O,S*-Dialkyl Dithiocarbonates (1):**

O,S-*Dimethyl Dithiocarbonate* (**1**; $R^1 = R^2 = CH_3$): Prepared by stirring at room temperature a mixture of potassium *O*-methyl dithiocarbonate (14.6 g, 0.1 mol), dimethyl sulfate (12.6 g, 0.1 mol) and sodium hydrogen carbonate (8.4 g, 0.1 mol) in water (100 ml). The reaction is completed after 15 min (^{1}H-N.M.R.; disappearance of dimethyl sulfate).

O,S-*Diethyl Dithiocarbonate* (**1**; $R^1 = R^2 = C_2H_5$). Prepared in the same way from potassium *O*-ethyl dithiocarbonate and diethyl sulfate; reaction time 90 min.

O,S-*Dibutyl*, O,S-*Dioctyl*, O,S-*Dibenzyl Dithiocarbonates* (**1**; $R^1 = R^2 = n$-C_4H_9, n-C_8H_{17}, C_6H_5-CH_2) *and* O-*Butyl* S-*Octyl Dithiocarbonate* (**1**;

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Table 1. *S,S*-Dialkyl Dithiocarbonates **2** from *O,S*-Dialkyl Dithiocarbonates **1**

R^1, R^2	Yield[a] [%]	b.p. [°C]/torr or m.p. [°C] found	reported	I.R. (film or CCl_4) ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4) δ [ppm]
CH_3	90	66–67°/21	58–59°/16[2]	see Ref.[5]	see Ref.[2]
C_2H_5	85	80–81°/16	83–86°/14[5]	see Ref.[5]	1.30 (t, CH_3); 2.95 (q, CH_2)
n-C_4H_9	76 (80)	137–138°/17	134–135°/16[2]	see Ref.[2,6]	see Ref.[2]
n-C_8H_{17}	79[b] (82)	177–178°/0.5	177–178°/0.5[2,7]	see Ref.[7]	see Ref.[7]
C_6H_5—CH_2	70[c] (72)	45–46°[d]	45–46°[2]	see Ref.[2]	see Ref.[2]

[a] The reported yields are of pure distilled or crystallized product. The yields reported in brackets are, instead, determined by G.L.C. analysis using a Perkin-Elmer Gas Chromatograph SIGMA 3 provided with a Chromatography Data Station SIGMA 10 (conditions: SE 30, 5% over Varaport 30; temperature program 100→250 °C).

[b] G.L.C. analysis of the crude reaction mixture shows the following products: octyl mercaptan (5%), dioctyl sulfide (10%), dioctyl disulfide (2%), and *S,S*-dioctyl dithiocarbonate (82%). The latter is isolated pure (^{1}H-N.M.R.; G.L.C.) by vacuum fractional distillation as indicated in the experimental part for *S,S*-dibutyl dithiocarbonate.

[c] G.L.C. analysis of the crude reaction mixture shows the following products: benzyl mercaptan (4%), dibenzyl sulfide (23%), and *S,S*-dibenzyl dithiocarbonate (72%). The separation is achieved by chromatography through a silica gel column, using petroleum ether as eluent.

[d] From ethanol.

Table 2. *O,S*-Dialkyl Dithiocarbonates **1**

R^1, R^2	Yield[a] [%]	b.p. [°C]/torr	Molecular formula[b] or Lit. b.p. [°C]/torr	I.R. (film) ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4) δ [ppm]
CH_3	88	57–58°/20	65°/20[9]	1220, 1070	2.52 (s, 3H); 4.14 (s, 3H)
C_2H_5	93	84°/20	42°/0.25[10]	1215, 1062	see Ref.[10]
n-C_4H_9	98	137–138°/17	117°/4[11]	1212, 1052	0.8–1.2 (m, 6H); 1.2–2.1 (m, 8H); 3.21 (t, 2H); 4.55 (t, 2H)
n-C_8H_{17}	97	178°/0.4	$C_{17}H_{34}OS_2$ (318.6)	1215, 1060	0.7–1.1 (m, 6H); 1.1–2.1 (m, 24H); 3.18 (t, 2H); 4.52 (t, 2H)
$C_6H_5CH_2$	96	—[c]	$C_{15}H_{14}OS_2$ (274.4)	1225, 1190, 1055	4.28 (s, 2H); 5.52 (s, 2H); 7.2–7.4 (m, 10H_{arom})
n-$C_8H_{17}S$, n-C_4H_9O	97	147–148°/0.5	$C_{13}H_{26}OS_2$ (262.5)	1210, 1060	0.7–1.0 (m, 6H); 1.0–1.9 (m, 16H); 2.95 (t, 2H); 4.42 (t, 2H)

[a] The reported yields are of pure distilled product.

[b] The microanalyses are in good accord with the calculated values (C, ±0.13; H, ±0.10; S, ±0.12).

[c] Purified by filtration through a short column of silica gel, using petroleum ether as eluent. It cannot be further purified by distillation, because of decomposition.

$R^1 = n$-C_8H_{17}, $R^2 = n$-C_4H_9): Prepared from the required halides (0.1 mol), the required potassium *O*-alkyl dithiocarbonates (0.1 mol), Aliquat 336 (3.3 g), and water (100 ml), according to the procedure previously reported[4]. For the preparation of *O,S*-dibenzyl dithiocarbonate, the reaction must be run in the presence of a smaller amount of Aliquat (1 g) and at 0–2 °C for 3 h.

S,S-Dibutyl Dithiocarbonate (2; $R^1 = R^2 = n$-C_4H_9); Typical Procedure:
A mixture of *O,S*-dibutyl dithiocarbonate (**1**; 20.6 g, 0.1 mol) and tricaprylmethylammonium chloride (Aliquat 336, Fluka; 3 g) [under the same conditions, benzyltriethylammonium chloride does not catalyze the reaction] is stirred and heated at 100 °C until the complete disappearance of the starting compound is observed by ^{1}H-N.M.R. analysis (about 90 min). After completion of the rearrangement, the mixture is filtered through a small layer of silica gel using petroleum ether as eluent to remove the catalyst. G.L.C. analysis of the residue (for conditions, see footnote[a] of Table 1) shows the following products: dibutyl sulfide (12%), dibutyl disulfide (2%), and *S,S*-dibutyl dithiocarbonate (80%). The latter component is normally isolated by vacuum fractional distillation through a Claisen flask; yield: 76%; b.p. 137–138 °C/17 torr (Ref.[2], b.p. 134–135 °C/16 torr). It is pure according to ^{1}H-N.M.R. and G.L.C. analysis.

S,S-Dioctyl and *S,S*-dibenzyl dithiocarbonates are also prepared in the same way (for details, see footnotes [b,c] of Table 1).

When $R^1 = R^2 = C_2H_5$, the amount of Aliquat 336 used for 0.1 mol (15 g) of *O,S*-diethyl dithiocarbonate is 1.2 g and the procedure is modified as follows: the reaction mixture is put in a flask equipped with a Spaltrohr Column (Fischer) and gradually heated, under stirring, to 100 °C over a period of 30 min [*Caution:* the heating of the reaction mixture must be gradual as indicated and the amount of Aliquat must be smaller than that normally used in the other cases, in order to moderate the reaction.] This temperature is maintained for another 60 min, until complete disappearance of **1** (^{1}H-N.M.R.). At this point, the apparatus is connected with a water pump and the pressure is reduced to 16 torr. Fractional distillation of the reaction mixture affords *S,S*-diethyl dithiocarbonate **2**. To complete the distillation, the external bath is heated to 120 °C. The collected product is pure according to ^{1}H-N.M.R. and G.L.C. analysis: yield 85%; b.p. 80–81 °C/16 torr (Ref.[2], b.p. 83–84 °C/14 torr).

When $R^1 = R^2 = CH_3$, the amount of Aliquat 336 used for 0.1 mol (12.2 g) of *O,S*-dimethyl dithiocarbonate is 0.2 g [*Caution:* as above]. The procedure is identical to that reported above for $R^1 = R^2 = C_2H_5$ with the only difference that the reaction mixture must be heated very slowly up to 90 °C over a period of 90 min. At this point the rearrangement is complete (^{1}H-N.M.R.) and the reaction mixture can be distilled under vacuum.

Direct Preparation of S,S-Dialkyl Dithiocarbonates (2) from Alkyl Halides and Potassium *O*-Alkyl Dithiocarbonates:

S,S-Dibutyl Dithiocarbonate (2; $R^1 = R^2 = n$-C_4H_9); Typical Procedure:
According to the general method previously reported for the preparation of *O,S*-dialkyl dithiocarbonates **1**[4], a mixture of butyl bromide (13.7 g, 0.1 mol), potassium *O*-butyl dithiocarbonate (18.8 g, 0.1 mol), Aliquat 336 (3.3 g), and water (100 ml) is vigorously stirred at room temperature for 25–30 min until complete disappearance of butyl bromide (G.L.C.). The mixture is extracted with ether which is dried and evaporated in vacuo. The residue, composed of *O,S*-dibutyl dithiocarbonate and catalyst,

is directly heated at 100 °C for 90 min, then worked-up as indicated above to afford pure *S,S*-dibutyl dithiocarbonate; yield: 76%.

Catalytic Rearrangement of *O*-Butyl *S*-Octyl Dithiocarbonate with Aliquat 336:

A mixture of *O*-butyl *S*-octyl dithiocarbonate (**1**; $R^1 = n\text{-}C_8H_{17}$, $R^2 = n\text{-}C_4H_9$; 13.1 g, 0.05 mol) and Aliquat 336 (1.5 g) is heated at 100 °C for 90 min and then worked-up as indicated above for the preparation of *S,S*-dibutyl dithiocarbonate. G.L.C. analysis of the crude reaction mixture shows the following products (yields in mmol), that are indicated in order of increasing retention times: dibutyl sulfide (1.0), octyl mercaptan (0.6), dibutyl disulfide (4.5), *S,S*-dibutyl dithiocarbonate (12.5), *S*-butyl *S*-octyl dithiocarbonate (19.8), dioctyl disulfide (0.6), and *S,S*-dioctyl dithiocarbonate (10.6).

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