The Phase-Transfer Synthesis of *O*,*S*-Dialkyl Dithiocarbonates from Alkyl Halides and Alkyl Methanesulfonates

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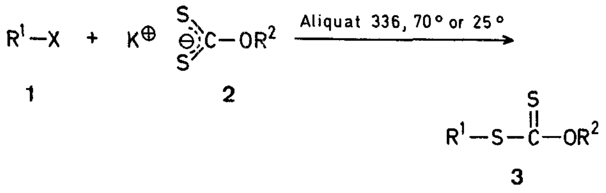
O,*S*-Dialkyl dithiocarbonates **3** have received much attention in connection with technological[1], biological[2,3,4], and synthetic applications[5-9]. The usual syntheses involve reactions between suitable alkali metal *O*-alkyl dithiocarbonates and alkyl halides in organic solvents such as acetone, alcohols, ethyl ether, toluene, etc., under reflux[5,10]. However these procedures frequently require long reaction times, varying from hours to days; this can be avoided by using aprotic polar solvents as dimethyl sulfoxide[11], dimethylformamide[8], or diglyme[9], but the latter are too expensive for large scale reactions.

In connection with previous results on the synthesis of alkanethiols from alkyl halides via *O*-*t*-butyl *S*-alkyl dithiocarbonates[9], we now wish to report a convenient procedure for synthesising **3** by reactions of primary and secondary alkyl halides or methanesulfonates with various potassium *O*-alkyl dithiocarbonates under phase-transfer conditions,

0039-7881/78/0532-0365 $ 03.00

in presence of tricaprylmethylammonium chloride (Aliquat 336) as catalyst.



The results are summarised in the Table. The reactions were carried out at two different temperatures (25° and/or 70°). At 25° the yields are slightly higher, but the reaction times drastically increase with less reactive alkyl derivatives. Except for highly reactive substrates, the more suitable reaction temperature therefore appears to be 70°.

The results of the reactions carried out at 25° clearly support a S_N2 mechanism in the organic phase, according to the following reactivity sequences: alkyl iodides > alkyl bromides > alkyl chlorides (entries 8, 10, 12; 16, 18, 19; 27, 29, 31; 35, 36), and primary alkyl halides and methanesulfonates > secondary alkyl halides and methanesulfonates (entries 8, 16; 10, 18; 12, 19; 29, 35; 31, 36; 14, 21; 33, 38). It should also be pointed out that the reactivity of dithiocarbonates **2**, by changing alkyl group R^2 follows the sequence: $CH_3 < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$ (entries 2, 10, 29, 40), which can be simply rationalised in terms of partition coefficients of reagents.

The present procedure for the synthesis of a wide variety of dithiocarbonates offers the following advantages: (a) short reaction times, (b) high yields, and (c), important for large scale reactions, low cost because of the absence of solvents.

All isolated *O*,*S*-dialkyl dithiocarbonates **3** were identified by microanalyses and I.R. spectra, and in some cases by comparison of b.p., I.R., and n_D data and G.L.C. or H.P.L.C. retention times with those of authentic samples prepared by known methods.

Alkyl halides were commercially available products (Fluka), with the exception of 2-chlorooctane and 2-iodooctane that were prepared according to the procedure described for the preparation of the corresponding optically active halides[12]; *n*-butyl, *n*-octyl, and 2-octyl methanesulfonates were prepared as in literature[13].

Potassium *O*-methyl, *O*-ethyl, *O*-*i*-propyl and *O*-octyl dithiocarbonates were prepared by standard procedures[5, 10] from potassium hydroxide or potassium metal (in the cases of *O*-*i*-propyl and *O*-octyl) with an excess of the alcohol required and then carbon disulfide. Potassium *O*-*t*-butyl dithiocarbonate was prepared as recently reported by us[9].

Preparation of *O*,*S*-Dialkyl Dithiocarbonates 3; General Procedure:

Alkyl halide or alkyl methanesulfonate **1** (50 mmol), potassium *O*-alkyl dithiocarbonate **2** (50 mmol), tricaprylmethylammonium chloride (Aliquat 336, Fluka; 1.68 g, 5 mmol), and water (50 ml) are combined and the yellow mixture is stirred vigorously at 70° or 25° until a yellow oil comes to the surface [only *O*-ethyl *S*-benzyl dithiocarbonate (**3h**) remains on the bottom], and the aqueous solution becomes completely colourless. The reaction times are reported in the Table. After cooling, petroleum ether (100–150 ml) is added and the organic layer is separated, dried, and filtered over a small layer of silica gel, using petroleum ether as eluent. The solvent is removed on a rotary evaporator and the residue is easily fractionated in vacuum or crystallised by acetone/methanol (see Table for yields and physical properties).

Pentane is used for the extraction of *O*-*t*-butyl *S*-octyl dithiocarbonate (**3n**) from the reaction mixture. In this case the following filtration over silica gel must be rapid because the cleavage of

Table. Dithiocarbonates **3a–n** prepared

Entry	Starting Materials R^1–X	R^2 in 2	Product
1	$n\text{-}C_8H_{17}-Br$	CH_3	**3a**
2			
3	$i\text{-}C_3H_7-J$	C_2H_5	**3b**
4	$n\text{-}C_4H_9-J$	C_2H_5	**3c**
5	$n\text{-}C_4H_9-Br$	C_2H_5	**3c**
6	$n\text{-}C_4H_9-OSO_2CH_3$	C_2H_5	**3c**
7	$n\text{-}C_8H_{17}-J$	C_2H_5	**3d**
8			
9	$n\text{-}C_8H_{17}-Br$	C_2H_5	**3d**
10			
11	$n\text{-}C_8H_{17}-Cl$	C_2H_5	**3d**
12			
13	$n\text{-}C_8H_{17}-OSO_2CH_3$	C_2H_5	**3d**
14			
15	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-J$	C_2H_5	**3e**
16			
17	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-Br$	C_2H_5	**3e**
18			
19	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-Cl$	C_2H_5	—[c]
20	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-OSO_2CH_3$	C_2H_5	**3e**
21			
22	$n\text{-}C_{16}H_{33}-Br$	C_2H_5	**3f**
23	$H_2C{=}CH-CH_2-Cl$	C_2H_5	**3g**
24	$C_6H_5-CH_2-Cl$	C_2H_5	**3h**
25	C_2H_5-J	$n\text{-}C_8H_{17}$	**3i**
26	$n\text{-}C_{16}H_{33}-Br$	$n\text{-}C_8H_{17}$	**3j**
27	$n\text{-}C_8H_{17}-J$	$i\text{-}C_3H_7$	**3k**
28	$n\text{-}C_8H_{17}-Br$	$i\text{-}C_3H_7$	**3k**
29			
30	$n\text{-}C_8H_{17}-Cl$	$i\text{-}C_3H_7$	**3k**
31			
32	$n\text{-}C_8H_{17}-OSO_2CH_3$	$i\text{-}C_3H_7$	**3k**
33			
34	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-Br$	$i\text{-}C_3H_7$	**3l**
35			
36	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-Cl$	$i\text{-}C_3H_7$	—[c]
37	$C_6H_{13}-\overset{\overset{CH_3}{\mid}}{C}H-OSO_2CH_3$	$i\text{-}C_3H_7$	**3l**
38			
39	$n\text{-}C_{16}H_{33}-Br$	$i\text{-}C_3H_7$	**3m**
40	$n\text{-}C_8H_{17}-Br$	$t\text{-}C_4H_9$	**3n**

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

[b] The microanalyses are in good accord with the calculated values (C, ±0.18; H, ±0.24; S, ±0.21).

[c] No reaction at 25° or 70°.

Reaction time (min)/temp.	Yield[a] [%]	b.p./torr or m.p.	Lit. b.p./torr or Molecular formula[b]	$n_D^{20°}$	Lit. $n_D^{20°}$	I.R. (film) ν_{max} [cm^{-1}][c]	
5/70°	60	124°/1	$C_{10}H_{20}OS_2$ (220.40)	1.5126		1070	1218
25/25°	70						
5/70°	88	100°/26	86–90°/14[2]	1.5258	1.5231 (25°)[2]	1045	1218
5/70°	91	120°/20	125–130°/25[6]	1.5238	1.5228[6]	1048	1212
5/70°	85	120°/20		1.5238			
5/70°	82	120°/20		1.5238			
5/70°	91	125°/0.5	162–165°/10[6]	1.5080	1.5070[6]	1052	1212
10/25°	93						
5/70°	85	125°/0.5		1.5080			
20/25°	90						
45/70°	47–53	125°/0.5		1.5083			
48 h/25°	58						
5/70°	86	125°/0.5		1.5080			
60/25°	90						
10/70°	81	113–114°/0.5	$C_{11}H_{22}OS_2$ (234.43)	1.5085		1058	1212
2 h/25°	80						
25/70°	60–66	113–114°/0.5		1.5085			
24 h/25°	68						
	—	—		—			
12/70°[d]	72	113–114°/0.5		1.5085			
16 h/25°	88						
5/70°	quant.	41–42[e]	$C_{19}H_{38}OS_2$ (346.65)			1058	1212
10/25°	91	99°/17	90–91°/6[3]	1.5505	1.5510[3]	1048	1210
10/25°	90	125°/0.5	173–175°/10[6]	1.6028	1.6018[6]	1048	1215
10/25°	81	127°/0.7	$C_{11}H_{22}OS_2$ (234.43)	1.5080		1065	1220
5/70°	92	25–26°[e]	$C_{25}H_{50}OS_2$ (430.81)			1052	1215
6/25°	86	126°/0.5	$C_{12}H_{24}OS_2$ (248.46)	1.5032		1042	1222
5/70°	94	126°/0.5		1.5032			
15/25°	88						
60/70°	83	126°/0.5		1.5032			
48 h/25°	87						
5/70°	86	126°/0.5		1.5032			
45/25°	80						
25/70°	86	116°/0.6	$C_{12}H_{24}OS_2$ (248.46)	1.5032		1038	1215
12 h/25°	88						
	—	—	—	—			
10/70°[d]	86	116°/0.6		1.5032			
8 h/25°	87						
5/70°	quant.	23–24°[e]	$C_{20}H_{40}OS_2$ (360.67)			1048	1230
5/25°[f]	93[g]		$C_{13}H_{26}OS_2$ (262.48)			1022	1262

[d] 2-Octyl methanesulfonate must be prepared immediately before use, and added to the reaction mixture previously heated at 70°.

[e] Crystallised from acetone/methanol.

[f] Stirring is continued for 5 min again until H.P.L.C. analysis shows the completely disappearance of the starting octyl bromide.

[g] Yield of crude product.

3n to octanethiol is catalysed by these conditions. The solvent is then evaporated under vacuo at 40–45° and the crude residue cannot be further purified because of decomposition. However, its I.R. spectrum is completely superimposable to that of a sample prepared independently from octyl bromide and potassium *O*-*t*-butyl dithiocarbonate in diglyme by the procedure previously reported for the preparation of *O*-*t*-butyl *S*-dodecyl dithiocarbonate[9]. The sample cannot be purified further; however microanalysis and I.R. spectrum of the crude product (yield 90%) confirm the assigned structure as *O*-*t*-butyl *S*-octyl dithiocarbonate (**3n**).

$C_{13}H_{26}OS_2$	calc.	C 59.49	H 9.98	S 24.43
(262.5)	found	59.15	9.74	24.19

I.R. (liquid film): ν_{max} = 1022, 1040, 1140, 1262, 1370, 1395, 1455, 2850, 2920, 2950 cm^{-1}.

All *O*,*S*-dialkyl dithiocarbonates **3** have strong I.R. absorption bands in the region of 1022–1070 cm^{-1} and 1210–1262 cm^{-1} (see the Table), in accordance with literature[11]; purities were confirmed by G.L.C. analysis in the cases of R^2 = methyl, ethyl (SE 30, 5% over Varaport 30) and by H.P.L.C. analysis in the cases of R^2 = *i*-propyl, *t*-butyl (Waters 6000, μ-porasil column, hexane elution, r.i. detection)[14].

We thank the C.N.R. for financial support.

Received: January 16, 1978

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[14] In these cases G.L.C. analysis shows a partial (when R^2 = *i*-propyl) or total thermal decomposition (when R^2 = *t*-butyl)[9] of dithiocarbonates in the gas chromatograph column.

0039-7881/78/0532-0368 $ 03.00