Phase-Transfer Synthesis of Symmetrical and Unsymmetrical Dialkyl Trithiocarbonates[1]

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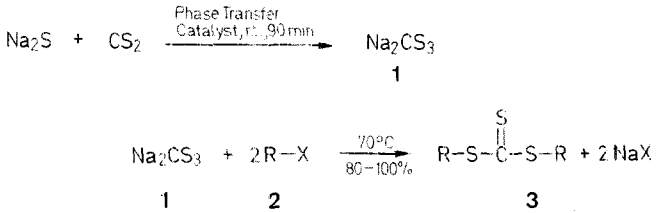
Symmetrical and unsymmetrical dialkyl trithiocarbonates having the formula $R^1S-CS-SR^2$ (wherein $R^1 = or \neq R^2$ were prepared under phase-transfer catalytic conditions by one-pot reactions involving carbon disulfide, sodium sulfide, alkyl halides, and alkyl mercaptans.

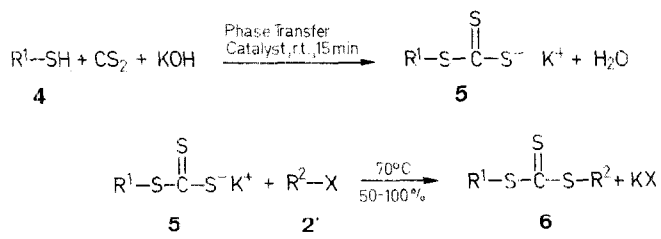
Symmetrical and unsymmetrical dialkyl trithiocarbonates constitute an important class of compounds which have been claimed for various applications, especially as pesticides in agriculture[2-11] and as lubricating additives[6,9,10,12-18]. The title compounds are usually prepared following two main synthetic routes: one- or two-step reaction of thiophosgene with suitable thiols[9,19-24]; alkylation of sodium or potassium salts of trithiocarbonic or alkyl trithiocarbonic acids for symmetrical or unsymmetrical compounds, respectively[3-10,15,19,25-28]. The first route utilizes poisonous thiophosgene as starting material; the second, in general, requires the use of organic solvents and gives the desired products in moderate yields.

In order to prepare large amount of the title compounds, we have now reinvestigated the second approach introducing the phase-transfer catalytic conditions. Thus, several symmetrical and unsymmetrical dialkyl trithiocarbonates **3** and **6** were prepared by one-pot procedures according to Scheme **A** and to Scheme **B**, respectively.



Scheme **A**

2,3	R	2,3	R
a	i-C_3H_7	**h**	n-$C_{18}H_{37}$
b	n-C_4H_9	**i**	$C_6H_5CH_2$
c	$CH_3(CH_2)_2CH(CH_3)$	**j**	4-$ClC_6H_4CH_2$
d	c-C_5H_9	**k**	4-t-$C_4H_9C_6H_4CH_2$
e	n-C_8H_{17}	**l**	$CH_2=CHCH_2$
f	$CH_3(CH_2)_5CH(CH_3)$	**m**	$-CH_2CH_2-$
g	n-$C_{12}H_{25}$		



Scheme **B**

The procedure for **3** involved two steps carried out in the presence of a phase-transfer catalyst, like Aliquat 336, Tetrabutylammonium bromide or Hexadecyltributylphosphonium bromide. In the first step sodium trithiocarbonate **(1)** was prepared by the reaction of aqueous sodium sulfide with carbon disulfide at room temperature for 90 min. It is noteworthy that in the absence of the catalyst the same reaction requires 18 hours at room temperature[29] or 7 hours at reflux[30]. In the second step dialkyl trithiocarbonates **3** were generated at 70 °C by bis-alkylation of the preformed aqueous sodium trithiocarbonate **(1)**. Procedure for trithiocarbonates **6** was similar; first potassium alkyltrithiocarbonates **5** were prepared *in situ* by the reaction of thiols **4** with carbon disulfide in aqueous potassium hydroxide, then **6** were obtained at 70 °C by mono-alkylation of the preformed salts **5**. Both steps were carried out in the presence of the abovementioned phase-transfer catalysts.

The results corresponding to symmetrical and unsymmetrical compounds are summarized in Table 1 and Table 2. Evidently, the application of the phase-transfer catalytic technique has drastic effects on the reactions investigated. In contrast with results obtained under previously established conditions, yields were excellent in all cases and reaction times were short, especially for unsymmetrical trithiocarbonates. Thus, for instance, the reaction of potassium trithiocarbonate with octadecyl chloride in ethanol at reflux for 8 hours under nitrogen afforded dioctadecyl trithiocarbonate in 41% yield[15]; the same product was obtained under phase-transfer conditions after 3 hours in quantitative yield (Table 1).

Similarly, benzyl t-butyl trithiocarbonate was obtained by a two-step reaction in water without catalyst after 3 hours (1 hour for the preparation of potassium t-butyl trithiocarbonate plus 2 hours for the benzylation reaction) in 18% yield[3]; however, the same trithiocarbonate was produced under phase-transfer conditions after 30 min (15 min for the first step plus 15 min for the second) in 97% yield (Table 2). This latter example shows that the phase-transfer catalyst is active in both steps of the reaction. In particular, the alkylation step exhibits the typical behaviour of the reactions carried out under phase-transfer catalytic conditions, according to the following reactivity sequences: primary alkyl halides > secondary alkyl halides and alkyl bromides > alkyl chlorides > alkyl iodides for symmetrical trithiocarbonates and alkyl iodides > alkyl bromides > alkyl chlorides for unsymmetrical trithiocarbonates. In the case of alkyl iodides, their reversed reactivity for two reaction series can be simply explained in terms of partition coefficients of the reagents. Likely, in the first series, iodide anions are more lipophilic than trithiocarbonate anions and tend to poison the phase transfer catalyst; on the contrary, in the second series, iodide anions are less lipophilic than alkyl trithiocarbonate anions and the reactions proceed quickly. Further, it can be observed that yields and reaction times are weakly affected by the different structure of the three catalysts examined.

In conclusion, the phase-transfer procedure reported here for the preparation of a wide variety of symmetrical and unsymmetrical trithiocarbonates offers some distinct advan-

Table 1. Symmetrical Dialkyl Trithiocarbonates **3a–m** Prepared

Product No.	Reaction Conditions			Yield[b] [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular Formula[c] or Lit. Data
	X in **2**	Phase-Transfer Catalyst[a] (g)	Time [h] at 70°C			
3a	Br	A(1)	2	90	33 (C_2H_5OH)	32[7]
3a	I	H(1)	4	91		
3b	Br	A(0.2)	1	90	131/0.5	106–108/0.4[7]
3c	Br	A(1)	6	90	130/0.5	$C_{11}H_{22}S_3$[d] (250.5)
		T(1)	6	90		
		H(1)	2	94		
3d	Br	A(0.2)	3	95	165/0.6	150–151/0.6[10]
		H(1)	1	90		
3e	Cl	A(1)	7	92	190–193/0.3	$C_{17}H_{34}S_3$[e] (334.6)
		T(1)	7	90		
		H(1)	5	96		
3e	Br	A(0.2)	1.5	~100		
		T(1)	3	97		
3e	I	A(1)	8	90		
3f	I	H(1)	14	80	167/0.3	$C_{17}H_{34}S_3$[f] (334.6)
3g	Br	A(0.2)	1.5	97	54 (CCl_4/CH_3OH)	52–52.5[22]
3h	Br	A(0.2)	3	~100	73–74 (CCl_4/CH_3OH)	69[15]
3i	Cl	A(0.2)	1	91	29 (C_2H_5OH)	28[7]
3j	Cl	A(0.2)	0.25	98	75 (CCl_4/CH_3OH)	71.5–72[31]
3k	Br	A(0.2)	0.5	~100	–[g]	$C_{22}H_{30}S_3$[h] (402.7)
3l	Cl	A(0.2)	2(r.t.)	90	100/0.3	77–78/0.3[9]
	Br	A(0.2)	0.25	90		
3m	1,2-di-Cl	A(0.2)	1.5	93[i]	36 (C_2H_5OH)	33–34[7]

[a] A = Aliquat 336 (Fluka); H = Hexadecyltributylphosphonium bromide (Fluka); T = Tetrabutylammonium bromide (Fluka). The amount of catalyst is referred to 0.2 mol of halide **2** (see experimental part).

[b] Yield of pure isolated product.

[c] Satisfactory microanalyses obtained: C ±0.15, H ±0.12, S ±0.12.

[d] ^{1}H-NMR (CCl_4): δ = 0.70–1.15 [m, 6H, $2CH(CH_3)-(CH_2)_2-CH_3$]; 1.15–2.00 [m, 8H, $2CH(CH_3)-(CH_2)_2-CH_3$]; 1.35 [d, 6H, $2CH(CH_3)-C_3H_7$, J = 7 Hz]; 3.80–4.40 ppm [m, 2H, $2CH(CH_3)-C_3H_7$].

[e] ^{1}H-NMR (CCl_4): δ = 0.70–1.10 [m, 6H, $2(CH_2)_7-CH_3$]; 1.10–1.90 [m, 24H, $2CH_2-(CH_2)_6-CH_3$]; 3.30 ppm (t, 4H, $2CH_2-C_7H_{15}$, J = 7 Hz).

[f] ^{1}H-NMR (CCl_4): δ = 0.70–1.15 [m, 6H, $2CH-(CH_3)-(CH_2)_5-CH_3$]; 1.15–2.00 [m, 20H, $2CH(CH_3)-(CH_2)_5-CH_3$]; 1.35 [d, 6H, $2CH(CH_3)-C_6H_{13}$, J = 7 Hz]; 3.80–4.40 ppm [m, 2H, $2CH(CH_3)-C_6H_{13}$].

[g] Viscous oil. It cannot be further purified by distillation because of decomposition.

[h] ^{1}H-NMR (CCl_4): δ = 1.35 (s, 18H, $2t$-C_4H_9); 4.50 (s, 4H, $2CH_2$); 7.22 ppm (s, 8H_{arom}).

[i] Ethylene trithiocarbonate obtained starting from 1,2-dichloroethane. Ratio carbon disulfide : sodium sulfide : 1,2-dichloroethane = 1 : 1 : 1.

tages over procedures usually employed. The advantages chiefly important for large scale production are met with, e.g.: absence of organic solvents, mild conditions, short reaction times and excellent yields.

All symmetrical and unsymmetrical trithiocarbonates **3** and **6** were identified by microanalyses, IR and ^{1}H-NMR spectra and, in most of the cases, also by comparison of their b.p., m.p. and GC retention times with those of authentic samples of analytical purity.

Dioctyl Trithiocarbonate (3c; R = n-C_8H_{17}); Typical Procedure[33]: A mixture of sodium sulfide nonahydrate (24 g, 0.1 mol), carbon disulfide (7.6 g, 0.1 mol) and tricaprylmethylammonium chloride (Aliquat 336; 0.2 g) in water (30 ml) is vigorously stirred at room temperature for 90 min. To the red solution of sodium trithiocarbonate so obtained, octyl bromide (**2**; R = n-C_8H_{17}, X = Br; 38.6 g, 0.2 mol) is added in one portion and under stirring. The temperature of the mixture is then slowly raised to 70°C in 15–20 min and maintained for an additional 90 min until the aqueous solution becomes completely colorless. After cooling, petroleum ether (150–200 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 to afford, with quantitative yield, virtually pure dioctyl trithiocarbonate according to ^{1}H-NMR, TLC and GC analysis (SE 30, 5% over Varaport 30; temperature program 100 to 250°C); b.p. 190–193°C/0.3 torr (Table 1).

$C_{17}H_{34}S_3$	calc.	C 61.02	H 10.24	S 28.74
(334.6)	found	61.14	10.36	28.70

Instead of filtration on silica gel, the product can be separated from the catalyst simply by distillation under *vacuo*.

A proof run in the absence of phase-transfer catalyst gave the following results: the aqueous solution became colourless after 40 h of heating at 70°C and the reaction mixture, worked up as above

Table 2. Dialkyl Trithiocarbonates **6a–v** Prepared

Product No.	R^1 in **4** and **6**	R^2 in **2′** and **6**	Reaction Conditions			Yield[b] [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular Formula[c] or Lit. Data	^{1}H-NMR (CCl_4/TMS) δ [ppm][d]
			X in **2′**	Phase-Transfer Catalyst[a] [g]	Time [min. or h]				
6a	i-C_3H_7	n-C_8H_{17}	Br	A(0.2)	15	~100	142–144/0.3	$C_{12}H_{24}S_3$ (264.5)	0.70–1.10 [m, 3H, $(CH_2)_7-CH_3$]; 1.10–2.00 [m, 12H, $CH_2-(CH_2)_6-CH_3$]; 1.40 [d, 6H, J = 7 Hz, $CH(CH_3)_2$]; 3.30 [t, 2H, J = 7 Hz, $CH_2-C_7H_{15}$]; 3.80–4.40 [m, 1H, $CH(CH_3)_2$]
				T(0.2)	30	95			
6b	n-C_4H_9	n-C_4H_9	Br	A(0.2)	15	95	131/0.5	106–108/0.4[7]	
6c	n-C_4H_9	c-C_5H_9	Br	A(0.2)	90	90	138–139/0.3	$C_{10}H_{18}S_3$ (234.4)	0.75–1.15 [m, 3H, $(CH_2)_3-CH_3$]; 1.15–2.45 [m, 12H, $CH_2-(CH_2)_2-CH_3$ and 4CH_2-cyclo]; 3.30 [t, 2H, J = 7 Hz, $CH_2-C_3H_7$]; 3.95–4.45 (m, 1H, CH-cyclo)
6d	n-C_4H_9	$CH_3(CH_2)_2CH(CH_3)$	Br	A(1)	2 h	94	117/0.3	$C_{10}H_{20}S_3$ (236.5)	0.70–1.20 [m, 6H, $(CH_2)_3-CH_3$ and $CH(CH_3)-(CH_2)_2-CH_3$]; 1.20–2.10 [m, 8H, $CH_2-(CH_2)_2-CH_3$ and $CH(CH_3)-(CH_2)_2-CH_3$]; 3.37 [d, 3H, J = 7 Hz, $CH(CH_3)-C_3H_7$]; 3.30 [t, 2H, J = 7 Hz, $CH_2-C_3H_7$]; 3.85–4.40 [m, 1H, $CH(CH_3)-C_3H_7$]
				H(1)	2 h	93			
6e	n-C_4H_9	n-C_8H_{17}	Cl	A(1)	7 h	80	173–174/0.4	$C_{13}H_{26}S_3$ (278.5)	0.70–1.15 [m, 6H, $(CH_2)_3-CH_3$ and $(CH_2)_7-CH_3$]; 1.15–2.00 [m, 16H, $CH_2-(CH_2)_2-CH_3$ and $CH_2-(CH_2)_6-CH_3$]; 3.32 [t, 4H, J = 7 Hz, $CH_2-C_3H_7$ and $CH_2-C_7H_{15}$]
				T(1)	5 h	87			
				H(1)	4 h	81			
6e	n-C_4H_9	n-C_8H_{17}	Br	A(0.2)	15	98			
				T(0.2)	30	96			
6e	n-C_4H_9	n-C_8H_{17}	I	A(0.2)	5	~100			
				T(0.2)	15	~100			
6f	n-C_4H_9	$CH_3(CH_2)_5CH(CH_3)$	Br	A(1)	5 h	90	154–155/0.4	$C_{13}H_{26}S_3$ (278.5)	0.70–1.15 [m, 6H, $(CH_2)_3-CH_3$ and $CH(CH_3)-(CH_2)_5CH_3$]; 1.15–2.00 [m, 14H, $CH_2-(CH_2)_2-CH_3$ and $CH(CH_3)-(CH_2)_5-CH_3$]; 1.35 [d, 3H, J = 7 Hz, $CH(CH_3)-C_6H_{13}$]; 3.32 [t, 2H, J = 7 Hz, $CH_2-C_3H_7$]; 3.80–4.35 [m, 1H, $CH(CH_3)-C_6H_{13}$]
6f	n-C_4H_9	$CH_3(CH_2)_5CH(CH_3)$	I	A(1)	20	~100			
6g	n-C_4H_9	n-$C_{12}H_{25}$	Cl	A(1)	10 h	89	196/0.3	$C_{17}H_{34}S_3$ (334.6)	0.70–1.15 [m, 6H, $(CH_2)_3-CH_3$ and $(CH_2)_{11}-CH_3$]; 1.15–1.95 [m, 24H, $CH_2-(CH_2)_2-CH_3$ and $CH_2-(CH_2)_{10}-CH_3$]; 3.32 [t, 4H, J = 7 Hz, $CH_2-C_3H_7$ and $CH_2-C_{11}H_{23}$]
				T(1)	10 h	86			
				H(1)	8 h	90			
6h	n-C_4H_9	n-$C_{16}H_{33}$	Br	A(0.2)	30	~100	42 ($CHCl_3$/CH_3OH)	$C_{21}H_{42}S_3$ (390.8)	0.75–1.10 [m, 6H, $(CH_2)_3-CH_3$ and $(CH_2)_{15}-CH_3$]; 1.10–1.95 [m, 32H, $CH_2-(CH_2)_2-CH_3$ and $CH_2-(CH_2)_{14}-CH_3$]; 3.32 [t, 4H, J = 7 Hz, $CH_2-C_3H_7$ and $CH_2-C_{15}H_{31}$]

Table 2. (Continued)

Product No.	R^1 in **4** and **6**	R^2 in **2′** and **6**	Reaction Conditions: X in **2′**	Phase-Transfer Catalyst[a] [g]	Time [min. or h]	Yield[b] [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular Formula[c] or Lit. Data	^{1}H-NMR (CCl_4/TMS) δ [ppm][d]
6i	n-C_4H_9	$C_6H_5CH_2$	Cl	A(0.2)	15	~100	156/0.3	167–170/3[32]	
6j	t-C_4H_9	n-C_4H_9	Br	A(0.2)	15	92	100/0.3	$C_9H_{18}S_3$ (222.4)	0.75–1.15 [m, 3H, $(CH_2)_3-CH_3$]; 1.20–1.90 [m, 4H, $CH_2-(CH_2)_2-CH_3$]; 1.62 (s, 9H, t-C_4H_9); 3.25 (t, 2H, J = 7 Hz, $CH_2-C_3H_7$)
6k	t-C_4H_9	n-C_8H_{17}	Br	A(0.2)	15	96	157–160/0.4	$C_{13}H_{26}S_3$ (278.5)	0.75–1.10 [m, 3H, $(CH_2)_7-CH_3$]; 1.10–1.90 [m, 12H, $CH_2-(CH_2)_6-CH_3$]; 1.62 (s, 9H, t-C_4H_9); 3.25 (t, 2H, J = 7 Hz, $CH_2-C_7H_{15}$)
6l	t-C_4H_9	n-$C_{16}H_{33}$	Br	A(0.2)	15	95	51 (CCl_4/CH_3OH)	$C_{21}H_{42}S_3$ (390.8)	0.75–1.10 [m, 3H, $(CH_2)_{15}-CH_3$]; 1.10–1.90 [m, 28H, $CH_2-(CH_2)_{14}-CH_3$]; 1.62 (s, 9H, t-C_4H_9); 3.25 (t, 2H, J = 7 Hz, $CH_2-C_{15}H_{31}$)
6m	t-C_4H_9	$C_6H_5CH_2$	Cl	A(0.2)	15	97	155/0.3	220–223/1.8[3]	
6c	n-C_8H_{17}	n-C_4H_9	Br	A(0.2)	15	98			
6n	n-C_8H_{17}	n-C_8H_{17}	Br	A(0.2)	15	~100	190–193/0.3	$C_{17}H_{34}S_3$ (334.6)	0.70–1.10 [m, 6H, $2(CH_2)_7-CH_3$]; 1.10–1.90 [m, 24H, $2CH_2-(CH_2)_6-CH_3$]; 3.30 (t, 4H, J = 7 Hz, $2CH_2-C_7H_{15}$)
6o	n-C_8H_{17}	$C_6H_5CH_2$	Cl	A(0.2)	15	~100	188/0.3	$C_{16}H_{24}S_3$ (312.6)	0.70–1.10 [m, 3H, $(CH_2)_7-CH_3$]; 1.10–1.90 [m, 12H, $CH_2-(CH_2)_6-CH_3$]; 3.30 (t, 2H, J = 7 Hz, $CH_2-C_7H_{15}$); 4.50 (s, 2H, $CH_2-C_6H_5$); 7.20 (m, $5H_{arom}$)
6p	n-$C_{12}H_{25}$	i-C_3H_7	Br	A(1)	3 h	97	180/0.3	$C_{16}H_{32}S_3$ (320.6)	0.75–1.10 [m, 3H, $(CH_2)_{11}-CH_3$]; 1.10–1.90 [m, 20H, $CH_2-(CH_2)_{10}-CH_3$]; 1.40 [d, 6H, J = 7 Hz, $CH(CH_3)_2$]; 3.30 [t, 2H, $CH_2-C_{11}H_{23}$]; 3.90–4.40 [m, 1H, $CH(CH_3)_2$]
6q	n-$C_{12}H_{25}$	$CH_2=CH-CH_2$	Cl	A(0.2)	90[e]	94	190/0.3	$C_{16}H_{30}S_3$ (318.6)	0.70–1.05 [m, 3H, $(CH_2)_{11}-CH_3$]; 1.05–1.90 [m, 20H, $CH_2-(CH_2)_{10}-CH_3$]; 3.32 (d, 2H, J = 7 Hz, $CH_2-C_{11}H_{23}$); 3.95 (d, 2H, J = 7 Hz, CH_2); 4.98 6.10 (m, 3H, $CH=CH_2$)
6q	n-$C_{12}H_{25}$	$CH_2=CH-CH_2$	Br	A(0.2)	30[e]	~100			
6h	n-$C_{16}H_{33}$	n-C_4H_9	Br	A(0.2)	15	98			
6r	n-$C_{16}H_{33}$	$C_6H_5CH_2$	Cl	A(0.2)	15	~100	54 (CCl_4/CH_3OH)	$C_{24}H_{40}S_3$ (424.8)	0.75–1.05 [m, 3H, $(CH_2)_{15}-CH_3$]; 1.05–1.80 [m, 28H, $CH_2-(CH_2)_{14}-CH_3$]; 3.30 [t, 2H, J = 7 Hz, $CH_2-C_{15}H_{31}$]; 4.50 (s, 2H, $CH_2-C_6H_5$); 7.20 (m, $5H_{arom}$)
6i	$C_6H_5CH_2$	n-C_4H_9	Br	A(0.2)	15	98	156/0.3	167–170/3[32]	
6o	$C_6H_5CH_2$	n-C_8H_{17}	Br	A(0.2)	15	~100			
6s	C_6H_5	n-C_4H_9	Br	H(1)	15	50	140/0.3	$C_{11}H_{14}S_3$ (242.4)	0.75–1.15 [m, 3H, $(CH_2)_3-CH_3$]; 1.15–1.90 [m, 4H, $CH_2-(CH_2)_2-CH_3$]; 3.22 [t, 2H, J = 7 Hz, $CH_2-C_3H_7$]; 7.45 (m, $5H_{arom}$)

Table 2. (Continued)

Product No.	R^1 in **4** and **6**	R^2 in **2'** and **6**	Reaction Conditions			Yield[b] [%]	m.p. [°C] (solvent) or b.p. [°C]/torr	Molecular Formula[c] or Lit. Data	^{1}H-NMR (CCl_4/TMS) δ [ppm][d]
			X in **2'**	Phase-Transfer Catalyst[a] [g]	Time [min. or h]				
6t	Benzo-thiazolyl	*n*-C_4H_9	Br	H(1)	15	50	125–126/0.3	$C_{12}H_{13}NS_4$ (299.5)	0.75–1.15 [m, 3H, $(CH_2)_3-CH_3$]; 1.15–2.05 [m, 4H, $CH_3-(CH_2)_2-CH_2$]; 3.32 [t, 2H, $J = 7$ Hz, $CH_2-C_3H_7$]; 6.95–7.50, 7.50–7.75 (2m, $4H_{arom}$)
6u	*n*-C_4H_9	CH_2	Br_2	A(0.2)[f]	15	95	25 (CCl_4/CH_3OH)	$C_{11}H_{20}S_6$ (344.6)	0.75–1.15 [m, 6H, $2(CH_2)_3-CH_3$]; 1.15–2.00 [m, 8H, $2CH_2-(CH_2)_2-CH_3$]; 3.35 [t, 4H, $J = 7$ Hz, $2CH_2-C_3H_7$]; 5.20 (s, 2H, $S-CH_2-S$)
6v	*n*-C_8H_{17}	CH_2	Br_2	A(0.2)[f]	15	95	42–43 (CCl_4/CH_3OH)	$C_{19}H_{36}S_6$ (456.9)	0.75–1.10 [m, 6H, $2(CH_2)_7-CH_3$]; 1.10–2.00 [m, 24H, $2CH_2-(CH_2)_6-CH_3$]; 3.35 [t, 4H, $J = 7$ Hz, $2CH_2-C_7H_{15}$]; 5.20 (s, 2H, $S-CH_2-S$)

[a] A = Aliquat 336 (Fluka); H = Hexadecyltributylphosphonium bromide (Fluka); T = Tetrabutylammonium bromide (Fluka). The amount of catalyst is referred to 0.1 mol of R^1-SH **4** and 0.1 mol of R^2-X **2'**.

[b] Yield of pure isolated product.

[c] Satisfactory microanalyses obtained: C ± 0.14, H ± 0.12, S ± 0.13.

[d] Recorded with a Hitachi-Perkin Elmer R-24B spectrometer (60 MHz).

[e] Reactions carried out at room temperature.

[f] The reactions were carried out with the following ratio of the reagents: butyl or respectively octyl mercaptan (0.1 mol), carbon disulfide (0.1 mol), potassium hydroxide (20% in water, 31 ml), Aliquat 336 (0.2 g) and dibromomethane (0.05 mol).

described and monitored by GC showed the following composition: dioctyl trithiocarbonate (41% yield), starting octyl bromide (28%), octyl mercaptan (7%) and dioctyl disulfide (7%).

Butyl Octyl Trithiocarbonate (6c; $R^1 = n$-C_4H_9, $R = n$-C_8H_{17}); Typical Procedure[33]:

Carbon disulfide (7.6 g, 0.1 mol) and tricaprylmethylammonium chloride (Aliquat 336, 0.2 g) are added to a solution of butyl mercaptan (**4**; $R^1 = n$-C_4H_9; 9 g, 0.1 mol) in potassium hydroxide (20% in water, 31 ml). The mixture is vigorously stirred at room temperature for 15 min. To the orange solution of potassium butyl trithiocarbonate so obtained, octyl bromide (**2'**; $R^2 = n$-C_8H_{17}, X = Br; 19.3 g, 0.1 mol) is added in one portion and under stirring and the reaction mixture is then slowly heated up to 70°C over a period of 15–20 min. This temperature is maintained until the aqueous solution becomes colourless (15 min). GC analysis showed the complete disappearance of the starting butyl mercaptan and octyl bromide. After cooling, the reaction mixture is extracted with petroleum ether (150–200 ml), which is separated, dried and filtered over a small layer of silica gel using the same solvent as eluent. After evaporation *in vacuo*, virtually pure butyl octyl trithiocarbonate is obtained in 98% yield, purity control by ^{1}H-NMR and GC (SE 30, 5% over Varaport 30; temperature program 100 to 250°C); b.p. 173–174°C/0.4 torr (Table 2).

$C_{13}H_{26}S_3$ (278.5)	calc.	C 56.06	H 9.41	S 34.53
	found	56.20	9.53	34.62

Instead of filtration on silica gel, the product can be separated from the catalyst simply by distillation under *vacuo*.

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