Convenient Synthesis of Alkanediyl Bis(alkyl trithiocarbonate)s from Alkanedithiols with Alkyl Halides and Carbon Disulfide in the Presence of Phase-Transfer Catalyst

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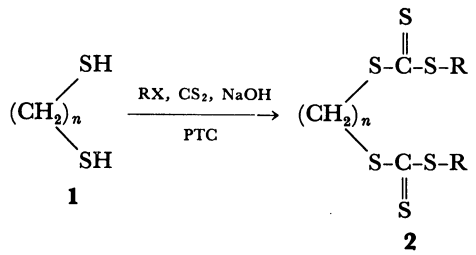
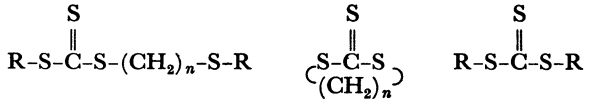
Synopsis. Alkanediyl bis(alkyl trithiocarbonate)s were conveniently synthesized by treating alkanedithiols with alkyl halides and carbon disulfide in the presence of a phase-transfer catalyst.

It is known that trithiocarbonates, R-S-C(=S)-S-R, exhibit insecticidal and fungicidal activities.[1] Therefore, many chemists have investigated the synthesis of trithiocarbonates, for example, by reactions of (i)sodium trithiocarbonate with alkyl halides,[2] (ii) thiophosgene with benzenethiols,[3] (iii)arylchlorodithioformates with alkanethiols,[4] (iv)lithium alkyltrithiocarbonates derived from lithio 2-alkylthio-1,3-dithiolanes with alkyl halides,[5] and (v)alkanethiols and haloalkanenitriles with carbon disulfide in the presence of tetrabutylammonium sulfate.[6] Recently, we also reported the one-pot synthesis of alkyl aryl trithiocarbonates by treating thiols with alkyl halides and carbon disulfide in the presence of a phase-transfer catalyst.[7] However, bis(trithiocarbonate)s, R-S-C(=S)-S-$(CH_2)_n$-S-C(=S)-S-R, which may have synthetic potential due to the presence of two trithiocarbonate groups are yet difficult to obtain. To our knowledge, there have been only two reports on the preparation of two 1,2-ethanediyl bis(alkyltrithiocarbonate)s from 2,2′-[1,2-ethanediylbis(thio)]bis[1,3-dithiolane].[8] Here, we wish to report a convenient preparation of (*S,S′*-)alkanediyl bis(alkyl trithiocarbonate)s (**2**) from α,ω-alkanedithiols (**1**) with alkyl halides and carbon disulfide in the presence of a phase-transfer catalyst (PTC) (Eq. 1).



1 **2** (1)

Since a marked difference was not observed in the use of other catalysts, we employed trioctylmethylammonium chloride as a phase-transfer catalyst. Various (*S,S′*-)alkanediyl bis(alkyl trithiocarbonate)s (**2aa–2de**) were synthesized from α,ω-alkanedithiols (**1**), for example, 1,2-ethane-, 1,3-propane- and 1,6-hexanedithiols, in good yields as shown in Table 1. The absence of PTC resulted in a poor yield of (*S,S′*-)alkanediyl bis(alkyl trithiocarbonate)s (**2**). All reactions proceeded smoothly at an ambient temperature.



3 **4** **5**

The use of alkyl iodides rather than bromides gave better results (Runs 5—6). Bulky alkyl iodides such as isopropyl iodide did not yield the desired (*S,S′*-)alkanediyl bis(alkyl trithiocarbonate)(**2**) (Run 10). It is noted that 1,6-hexanedithiol gave **2** selectively. Bis(trithiocarbonate)s **2ab–2ac** and **2ba–2de** obtained by this method were new compounds.

This novel method for the preparation of (*S,S′*-)alkanediyl bis(alkyl trithiocarbonate)s is convenient, and has synthetic utility.

Experimental

All Melting points were uncorrected. ^{1}H NMR spectra were measured with a HITACHI R-20B, using tetramethylsilane as internal standard. IR spectra were obtained on a JASCO-G spectrophotometer. Elemental analysis were determined with YANAGIMOTO MT-3.

General Procedure. To a solution of α,ω-alkanedithiol (**1**) (3.5 mmol) and sodium hydroxide (10.5 mmol) in water (5 ml), carbon disulfide (10.5 mmol) and trioctylmethylammonium chloride (0.07 mmol) was added and then stirred at 10—30 °C for 2 h. Alkyl halide (10.5 mmol) in benzene (5 ml) was added to the solution and further stirring was continued at the temperature for 3 h. After completion of the reaction benzene layer was washed with water and then dried on sodium sulfate. Yellow oil obtained by evaporation of benzene was chromatographed on silica gel using chloroform as eluent, to give the desired (*S,S′*-)alkanediyl bis(alkyl trithiocarbonate)s (**2**) together with by-products (**3**, **4**, and **5**). The structure of the products were characterized by ^{1}H NMR, IR, MS, and elemental analysis.

1,2-Ethanediyl Bis(methyl trithiocarbonate) 2aa: Mp 53.3 °C;[8] IR (KBr) 2900, 1380, 1040, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.75 (s, 6H, CH_3) and 3.67 (s, 4H, CH_2); Found: C, 26.38; H, 3.55%. Calcd for $C_6H_{10}S_6$: C, 26.25; H, 3.67%.

1,2-Ethanediyl Bis(ethyl trithiocarbonate) 2ab: Mp 35.0 °C; IR (KBr) 2900, 1383, 1058 and 805 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.38 (t, 6H, 7.2 Hz, CH_3), 3.35 (q, 4H, 7.2 Hz, CH_2) and 3.64 (s, 4H, CH_2); Found: C, 31.78; H, 4.62%. Calcd for $C_8H_{14}S_6$: C, 31.76; H, 4.66%.

1,2-Ethanediyl Bis(propyl trithiocarbonate) 2ac: Mp 32.0 °C; IR (KBr) 2900, 1390, 1039, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97 (t, 6H, 6.8 Hz, CH_3), 1.68 (m, 4H, 6.8, 7.2 Hz, CH_2), 3.25 (t, 4H, 7.2 Hz, CH_2) and 3.51 (s, 4H, CH_2); Found: C, 36.68; H, 5.30%. Calcd for $C_{10}H_{18}S_6$: C, 36.33; H, 5.49%.

1,2-Ethanediyl Bis(methoxycarbonylmethyl trithiocarbonate) 2ad: Mp 65.0 °C[8]; IR (KBr) 2900, 1730, 1160, and 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.70 (s, 4H, CH_2), 3.77 (s,

Table 1. Reaction of Alkanedithiols with Alkyl Halides and Carbon Disulfide in the Presence of PTC[a)]

Run	Alkanedithiol	Alkyl halide	React.		Yield of product/%[b)]			
			Temp/°C	Time/h	**2**	**3**	**4**	**5**
1	Ethane	CH_3I	10	3	82 (**2aa**)	10 (**3aa**)	8	Trace
2			r.t.	3	73 (**2aa**)	24 (**3aa**)	Trace	Trace
3			40	3	50 (**2aa**)	44 (**3aa**)	6	5
4[c)]			10	3	4 (**2aa**)	54 (**3aa**)	20	22
5		C_2H_5I	10	3	86 (**2ab**)	11 (**3ab**)	Trace	Trace
6		C_2H_5Br	10	3	35 (**2ab**)	36 (**3ab**)	29	27
7		n-C_3H_7I	20	5	45 (**2ac**)	8 (**3ac**)	45	20
8		n-C_3H_7Br	20	5	7 (**2ac**)	19 (**3ac**)	16	Trace
9		n-C_3H_7Cl	20	5	0	0	20	0
10		i-C_3H_7I	30	20	0	0	67	16
11		CH_3OCOCH_2Br	10	5	90 (**2ad**)	Trace	4	0
12	Propane	CH_3I	20	5	81 (**2ba**)	11 (**3ba**)	8	Trace
13		C_2H_5I	20	5	83 (**2bb**)	9 (**3bb**)	8	8
14		n-C_3H_7I	20	5	76 (**2bc**)	6 (**3bc**)	12	11
15		CH_3OCOCH_2Br	20	5	92 (**2bd**)	Trace	4	0
16		$C_6H_5CH_2Br$	20	5	83 (**2be**)	16 (**3be**)	Trace	Trace
17	Butane	CH_3I	20	5	86 (**2ca**)	12 (**3ca**)	Trace	Trace
18		C_2H_5I	20	5	87 (**2cb**)	12 (**3cb**)	Trace	Trace
19		n-C_3H_7I	20	5	78 (**2cc**)	10 (**3cc**)	Trace	Trace
20		CH_3OCOCH_2Br	20	5	90 (**2cd**)	8 (**3cd**)	Trace	0
21		$C_6H_5CH_2Br$	20	5	84 (**2ce**)	14 (**3ce**)	Trace	Trace
22	Hexane	CH_3I	20	3	100 (**2da**)	0	0	0
23		C_2H_5I	20	3	100 (**2db**)	0	0	0
24		n-C_3H_7I	20	8	96 (**2dc**)	0	0	0
25		CH_3OCOCH_2Br	20	3	91 (**2dd**)	Trace	6	0
26		$C_6H_5CH_2Br$	20	5	100 (**2de**)	0	0	0

a) Trioctylmethylammonium chloride was used as a PTC. b) Isolated yield. c) Reaction in the absence of PTC.

6H, CH_3) and 4.20 (s, 4H, CH_2); Found: C, 30.51; H, 3.88%. Calcd for $C_{10}H_{14}O_4S_6$: C, 30.75; H, 3.61%.

1,3-Propanediyl Bis(methyl trithiocarbonate) 2ba: Oil; IR (neat) 2890, 1405, 1070, and 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08 (quint, 2H, 7.0 Hz, CH_2), 2.72 (s, 6H, CH_3) and 3.45 (t, 4H, 7.0 Hz, CH_2); Found: C, 29.12; H, 4.09%. Calcd for $C_7H_{12}S_6$: C, 29.14; H, 4.19%.

1,3-Propanediyl Bis(ethyl trithiocarbonate) 2bb: Oil; IR (neat) 2910, 1446, 1252, 1075, and 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.34 (t, 6H, 7.2 Hz, CH_3), 2.07 (quint, 2H, 6.8 Hz, CH_2), 3.34 (t, 4H, 7.2 Hz, CH_2) and 3.43 (t, 4H, 6.8 Hz, CH_2); Found: C, 34.21; H, 4.95%. Calcd for $C_9H_{16}S_6$: C, 34.14; H, 5.09%.

1,3-Propanediyl Bis(propyl trithiocarbonate) 2bc: Oil; IR (neat) 2900, 1398, 1063, 1045, and 813 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (t, 6H, 6.8 Hz, CH_3), 1.68 (m, 4H, 6.8 Hz, 7.0 Hz, CH_2), 2.06 (quint, 2H, 7.0 Hz, CH_2), 3.32 (t, 4H, 7.0 Hz, CH_2) and 3.43 (t, 4H, 7.0 Hz, CH_2); Found: C, 38.29; H, 5.87%. Calcd for $C_{11}H_{20}S_6$: C, 38.33; H, 5.85%.

1,3-Propanediyl Bis(methoxycarbonylmethyl trithiocarbonate) 2bd: Mp 65.0 °C; IR (KBr) 2850, 1725, 1162, 1060, and 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.13 (m, 2H, 7.0 Hz, CH_2), 3.49 (t, 4H, 7.0 Hz, CH_2), 3.76 (s, 6H, CH_3) and 4.19 (s, 4H, CH_2); Found: C, 32.92; H, 3.91%. Calcd for $C_{11}H_{16}O_4S_6$: C, 32.65; H, 3.99%.

1,3-Propanediyl Bis(benzyl trithiocarbonate) 2be: Mp 58.0 °C; IR (KBr) 3040, 2900, 1450, 1073, 1060, 830, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.07 (quint, 2H, 7.0 Hz, CH_2), 3.43 (t, 4H, 7.0 Hz, CH_2), 4.59 (s, 4H, CH_2) and 7.25 (s, 10H, arom); Found: C, 51.58; H, 4.47%. Calcd for $C_{19}H_{20}S_6$: C, 51.78; H, 4.57%.

1,4-Butanediyl Bis(methyl trithiocarbonate) 2ca: Mp 54.9 °C; IR (KBr) 2900, 1407, 1065, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.78 (t, 4H, 6.0 Hz, CH_2), 2.69 (s, 6H, CH_3) and 3.36 (t, 4H, 6.0 Hz, CH_2); Found: C, 31.81; H, 4.44%. Calcd for $C_8H_{14}S_6$: C, 31.76; H, 4.66%.

1,4-Butanediyl Bis(ethyl trithiocarbonate) 2cb: Mp 34.0 °C; IR (KBr) 2920, 1448, 1073, 1022, and 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.33 (t, 6H, 7.2 Hz, CH_3), 1.78 (m, 4H, CH_2), 3.15—3.52 (m, 4H, CH_2) and 3.33 (q, 4H, 7.2 Hz, CH_2); Found: C, 36.64; H, 5.49%. Calcd for $C_{10}H_{18}S_6$: C, 36.33; H, 5.49%.

1,4-Butanediyl Bis(propyl trithiocarbonate) 2cc: Mp 27.4 °C; IR (KBr) 2930, 1448, 1075, 1022, and 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (t, 6H, 7.0 Hz, CH_3), 1.63 (sextet, 4H, 7.0 Hz, CH_2), 1.72 (t, 4H, 7.0 Hz, CH_2), 3.28 (t, 4H, 7.0 Hz, CH_2) and 3.31 (t, 4H, 7.0 Hz, CH_2); Found: C, 40.19; H, 5.94%. Calcd for $C_{12}H_{22}S_6$: C, 40.18; H, 6.18%.

1,4-Butanediyl Bis(methoxycarbonylmethyl trithiocarbonate) 2cd: Mp 66.2 °C; IR (KBr) 2860, 1746, 1165, and 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.80 (m, 4H, CH_2), 3.40 (m, 4H, CH_2), 3.74 (s, 6H, CH_3) and 4.15 (s, 4H, CH_2); Found: C, 34.65; H, 4.14%. Calcd for $C_{12}H_{18}O_4S_6$: C, 34.43; H, 4.33%.

1,4-Butanediyl Bis(benzyl trithiocarbonate) 2ce: Mp 95.5 °C; IR (KBr) 3010, 2900, 1452, 1052, 810, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.79 (m, 4H, CH_2), 3.39 (t, 4H, 6.5 Hz, CH_2), 4.60 (s, 4H, CH_2) and 7.38 (s, 10H, arom); Found: C, 52.53; H, 4.85%. Calcd for $C_{20}H_{22}S_6$: C, 52.58; H, 4.88%.

1,6-Hexanediyl Bis(methyl trithiocarbonate) 2da: Mp 72.0 °C; IR (KBr) 2900, 1409, 1262, 1064, and 808 cm^{-1};

^{1}H NMR ($CDCl_3$) δ=1.54 (m, 8H, CH_2), 2.77 (s, 6H, CH_3) and 3.39 (t, 4H, 8.0 Hz, CH_2); Found: C, 36.12; H, 5.32%. Calcd for $C_{10}H_{18}S_6$: C, 36.33; H, 5.49%.

1,6-Hexanediyl Bis(ethyl trithiocarbonate) 2db: Mp 42.0 °C; IR (KBr) 2910, 1410, 1250, 1089, and 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 (t, 6H, 7.2 Hz, CH_3), 1.44 (m, 8H, CH_2), 3.37 (q, 4H, 7.2 Hz, CH_2) and 3.35 (m, 4H, CH_2); Found: C, 40.39; H, 6.11%. Calcd for $C_{12}H_{22}S_6$: C, 40.19; H, 6.18%.

1,6-Hexanediyl Bis(propyl trithiocarbonate) 2dc: Mp 46.0 °C; IR (KBr) 2900, 1416, 1228, 1060, and 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (t, 6H, 7.0 Hz, CH_3), 1.53 (m, 8H, CH_2), 1.69 (sextet, 4H, 7.0 Hz, CH_2) and 3.35 (t, 8H, 7.0 Hz, CH_2); Found: C, 43.12; H, 6.65%. Calcd for $C_{14}H_{26}S_6$: C, 43.48; H, 6.78%.

1,6-Hexanediyl Bis(methoxycarbonylmethyl trithiocarbonate) 2dd: Mp 63.0 °C; IR (KBr) 2780, 1747, 1165, and 1076 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.50 (m, 8H, CH_2), 3.37 (t, 4H, CH_2), 3.74 (s, 6H, CH_3) and 4.17 (s, 4H, CH_2); Found: C, 37.40; H, 4.85%. Calcd for $C_{14}H_{22}O_4S_6$: C, 37.64; H, 4.96%.

1,6-Hexanediyl Bis(benzyl trithiocarbonate) 2de: Mp 86.0 °C; IR (KBr) 3010, 2920, 1454, 1060, 822, 798, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.50 (bs, 8H, CH_2), 3.35 (t, 4H, 7.0 Hz, CH_2), 4.60 (s, 4H, CH_2) and 7.28 (s, 10H, arom); Found: C, 54.62; H, 5.49%. Calcd for $C_{22}H_{26}S_6$: C, 54.73; H, 5.43%.

Methyl 2-(Methylthio)ethyl Trithiocarbonate 3aa: Oil; IR (neat) 2900, 1410, 1055, 1040, and 810 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ=2.17 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 2.70 (t, 2H, 7.8 Hz, CH_2) and 3.59 (t, 2H, 7.8 Hz, CH_2); Found: C, 30.04; H, 4.83%. Calcd for $C_5H_{10}S_4$: C, 30.28; H, 5.08%.

Ethyl 2-(Ethylthio)ethyl Trithiocarbonate 3ab: Oil; IR (neat) 2900, 1450, 1252, 1070, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.28 (t, 3H, 7.2 Hz, CH_3), 1.37 (t, 3H, 7.2 Hz, CH_3), 2.63 (q, 2H, 7.2 Hz, CH_2), 2.78 (t, 2H, 4.8 Hz, CH_2), 3.36 (q, 2H, 7.2 Hz, CH_2) and 3.56 (t, 2H, 4.8 Hz, CH_2); Found: C, 36.84; H, 6.12%. Calcd for $C_7H_{14}S_4$: C, 37.13; H, 6.23%.

Propyl 2-(Propylthio)ethyl Trithiocarbonate 3ac: Oil; IR (neat) 2900, 1054, 1039, and 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.99 (t, 3H, 6.8 Hz, CH_3), 1.01 (t, 3H, 6.8 Hz, CH_3), 1.62 (m, 2H, 6.8, 7.2 Hz, CH_2), 1.72 (m, 2H, 6.8, 7.2 Hz, CH_2), 2.54 (t, 2H, 7.2 Hz, CH_2), 2,80 (m, 2H, CH_2), 3.31 (t, 2H, 7.2 Hz, CH_2) and 3.50 (m, 2H, CH_2); Found: C, 42.21; H, 6.84%. Calcd for $C_9H_{18}S_4$: C, 42.48; H, 7.13%.

Methyl 3-(Methylthio)propyl Trithiocarbonate 3ba: Oil; IR (neat) 2880, 1417, 1070, and 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.03 (s, 3H, CH_3), 2.53 (quint, 2H, 7.0 Hz, CH_2), 2.72 (s, 3H, CH_3) and 3.46 (t, 4H, 7.0 Hz, CH_2); Found: C, 33.77; H, 5.53%. Calcd for $C_6H_{12}S_4$: C, 33.93; H, 5.70%.

Ethyl 3-(Ethylthio)propyl Trithiocarbonate 3bb: Oil; IR (neat) 2900, 1445, 1250, 1075, 1025, and 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22 (t, 3H, 7.0 Hz, CH_3), 1.34 (t, 3H, 7.0 Hz, CH_3), 1.92 (quint, 2H, 7.5 Hz, CH_2), 2.41 (t, 2H, 7.5 Hz, CH_2), 2.49 (q, 2H, 7.0 Hz, CH_2), 3.34 (q, 2H, 7.0 Hz, CH_2) and 3.44 (t, 2H, 7.5 Hz, CH_2); Found: C, 39.77; H, 6.56%. Calcd for $C_8H_{16}S_4$: C, 39.96; H, 6.71%.

Propyl 3-(Propylthio)propyl Trithiocarbonate 3bc: Oil; IR (neat) 2900, 1440, 1060, 1040, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.03 (t, 6H, 6.8 Hz, CH_3), 1.50—2.90 (m, 8H, 6.8, 7.0 Hz, CH_2), 3.32 (t, 4H, 7.0 Hz, CH_2) and 3.43 (t, 4H, 7.0 Hz, CH_2); Found: C, 44.61; H, 7.59%. Calcd for $C_{10}H_{20}S_4$: C, 44.73; H, 7.51%.

Benzyl 3-(Benzylthio)propyl Trithiocarbonate 3be: Oil; IR (neat) 3020, 2880, 1498, 1060, 798, and 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.00 (quint, 2H, 7.0 Hz, CH_2), 3.04 (t, 2H, 7.0 Hz, CH_2), 3.42 (t, 2H, 7.0 Hz, CH_2), 4.16 (s, 2H, CH_2), 4.54 (s, 2H, CH_2) and 7.18—7.21 (m, 10H, arom); Found: C, 59.33; H, 5.43%. Calcd for $C_{18}H_{20}S_4$: C, 59.30; H, 5.53%.

Methyl 4-(Methylthio)butyl Trithiocarbonate 3ca: Oil; IR (neat) 2920, 1420, 1065, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.67—1.84 (m, 4H, CH_2), 1.96 (s, 3H, CH_3), 2.40 (t, 2H, 7.0 Hz, CH_2), 2.66 (s, 3H, CH_3) and 3.32 (t, 2H, 7.0 Hz, CH_2); Found: C, 37.38; H, 6.18%. Calcd for $C_7H_{14}S_4$: C, 37.13; H, 6.23%.

Ethyl 4-(Ethylthio)butyl Trithiocarbonate 3cb: Oil; IR (neat) 2950, 1450, 1075, 1022, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.16 (t, 3H, 7.0 Hz, CH_3), 1.29 (t, 3H, 7.0 Hz, CH_3), 1.70 (m, 4H, CH_2), 2.41 (q, 2H, 7.0 Hz, CH_2), 2.42 (t, 2H, 7.0 Hz, CH_2), 3.29 (q, 2H, 7.0 Hz, CH_2) and 3.30 (t, 2H, 7.0 Hz, CH_2); Found: C, 42.28; H, 6.96%. Calcd for $C_9H_{18}S_4$: C, 42.48; H, 7.13%.

Propyl 4-(Propylthio)butyl Trithiocarbonate 3cc: Oil; IR (neat) 2920, 1455, 1060, 1038, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (t, 3H, CH_3), 1.28 (t, 3H, CH_3), 1.83 (m, 8H, CH_2), 2.80 (m, 2H, CH_2) and 3.39 (m, 6H, CH_2); MS (13.5 eV) *m/z* 283 (M^+), 239, 164, 120, and 43.

Methoxycarbonylmethyl 4-(Methoxycarbonylmethylthio)-butyl Trithiocarbonate 3cd: Mp 43.0 °C; IR (KBr) 2840, 1740, 1430, 1060, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.84 (m, 4H, CH_2), 3.44 (m, 4H, CH_2), 3.74 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 4.20 (s, 2H, CH_2) and 4.31 (s, 2H, CH_2); MS (10 eV) *m/z* 343 (M^+), 254, 193, 160, 91, and 74.

Benzyl 4-(Benzylthio)butyl Trithiocarbonate 3ce: Oil; IR (neat) 3020, 2900, 1450, 1060, and 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.63 (m, 4H, CH_2), 2.30 (m, 2H, CH_2), 3.26 (m, 2H, CH_2), 3.58 (s, 2H, CH_2), 4.52 (s, 2H, CH_2) and 7.17 (s, 10H, arom); Found: C, 60.57; H, 5.89%. Calcd for $C_{19}H_{22}S_4$: C, 60.27; H, 5.86%.

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