Convenient Synthesis of Cyclic Trithiocarbonates from 1,2- or 1,3-Dihaloalkanes and Sodium Trithiocarbonate in the Presence of Phase-Transfer Catalyst

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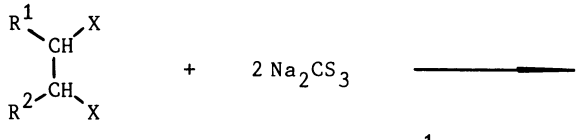
Synopsis. Cyclic trithiocarbonates, such as 1,3-dithiolane-2-thiones and 1,3-dithiane-2-thiones, were conveniently synthesized by treating 1,2- or 1,3-dihaloalkanes with sodium trithiocarbonate in the presence of a phase-transfer catalyst.

Much attention has been paid to the synthesis of cyclic trithiocarbonates, which are very important intermediates for the preparation of insecticides,[1] biologically active compounds[2] and the donor of a superconductor.[3] Many procedures for the synthesis of cyclic trithiocarbonates have hintherto been developed: for example, a reaction of potassium *O*-methyl dithiocarbonate or carbon disulfide with epoxide[4,5] a reaction of potassium *O*-methyl dithiocarbonate with 2-chloroethanols,[6] a reaction of sodium trithiocarbonate with 1,3-trimethylene dimesylates,[2] and a reaction of ammonium trithiocarbonates with α,ω-dithioalkanes.[7] These procedures have, however, some problems reparding the availability of the starting materials. In the course of our investigations on the synthesis of alkanediyl and alkyl aryl trithiocarbonates,[8] we found a convenient synthesis of cyclic trithiocarbonates, 1,3-dithiolane-2-thione (**2a—d**) and 1,3-dithiane-2-thione (**4a—c**), from 1,2- or 1,3-dihaloalkanes with sodium trithiocarbonate in phase-transfer catalyst (PTC) systems (Eqs. 1 and 2).

Trioctylmethylammonium chloride (TOMAC) was employed as a phase-transfer catalyst. As shown in Table 1, 1,3-dithiolane-2-thione (**2a**) was obtained in high yield from 1,2-dibromoethane (Run 4). The reaction in the absence of PTC resulted in a poor yeild of 4-methyl-1,3-dithiolane-2-thione (**2b**) (Runs 8—10). Surprisingly, 1,2-ethanedithiol also afforded 1,3-



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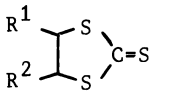

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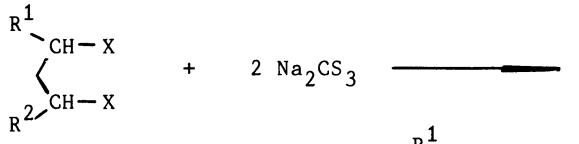

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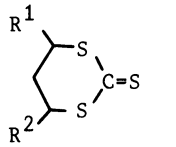


4 (2)

Table 1. Reaction of Substituted 1,2-Dihaloethane and Sodium Trithiocarbonate in the Presence of PTC

Run[a]	Substrate **1**			React		Catalyst	Yield of **2**	
	R^1	R^2	X	Temp/°C	Time/h	mmol	%[b]	
1	H	H	Br	60	8	0	84	**2a**
2	H	H	Br	60	8	0.02	92	**2a**
3	H	H	Br	60	3	0.02	76	**2a**
4	H	H	Br	60	8	0.08	97	**2a**
5[c]	H	H	SH	Reflux	2	0	90	**2a**
6	H	H	Cl	60	8	0.08	58	**2a**
7	H	H	I	60	8	0.08	—[d]	
8	CH_3	H	Br	60	8	0	25	**2b**
9	CH_3	H	Br	60	8	0.08	67	**2b**
10	CH_3	H	Br	60	20	0.08	81	**2b**
11	C_2H_5	H	Br	60	20	0.08	72	**2c**
12	CH_3	CH_3	Br	60	25	0.08	10	**2d**
13	C_6H_5	C_6H_5	Br	60	8	0.08	—[d]	

a) 1,2-Dihaloethane, 2 mmol; Na_2CS_3, 6 mmol. b) Isolated yield based on substrate. c) 1,2-Ethanedithiol, 2 mmol; CS_2, 6 mmol; NaOH, 2.5 mmol. d) Products were ethene derivatives.

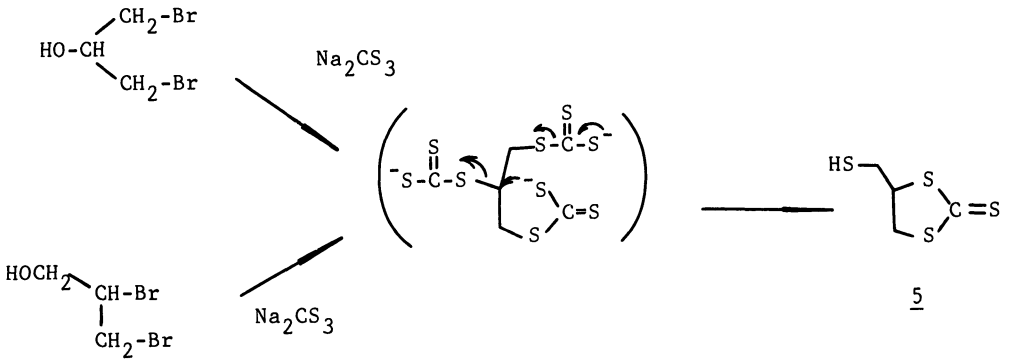
dithiolane-2-thione (**2a**) in high yield upon treating with carbon disulfide and sodium hydroxide, as shown in Table 1 (Run 5). It should be noted that the treatment of 1,2-diiodoethane and 1,2-dibromo-1,2-diphenylethane with sodium trithiocarbonate gave *trans*-1,2-diphenylethene, since the ethene was a dehalogenates product from the diiodide or dibromide (Runs 7 and 12).[9] Interestingly, 4-mercaptomethyl-1,3-dithiane-2-thione (**5**) was obtained in good yield upon treating 2,3-dibromo-1-propanol (59%) and 1,3-dibromo-2-propanol (37%) with sodium trithiocarbonate. The formation of **5** may be interpreted in terms of a substitution of the hydroxyl group with trithiocarbonate followed by cyclization as depicted in Scheme 1. The novel thiolane **5** is conceived to be a useful intermediate for the synthesis of biologically active compounds, based on previous results.[2]

Next, we studied the synthesis of 4-methyl-1,3-dithiane-2-thione (**4b**) by a reaction of 1,3-dibromobutane (**3**) with sodium trithiocarbonate in the presence of PTC. As shown in Table 2, three 1,3-dithiane-2-thiones (**4a—c**) were obtained in moderate yields. The treatment of 1,4-dibromobutane with sodium trithiocarbonate by the above-mentioned method was not prepared seven-membered cyclic trithiocarbonate.

As mentioned above, 1-3-dithiolane-2-thione **2** and 1,3-dithiane-2-thione **4** were synthesized in satisfactory yields by a reaction of the corresponding 1,2- or 1,3-dihaloalkanes with sodium trithiocarbonate in the presence of PTC. A plausible pathway for this reaction may be considered to be an internal nucleophillic attack of the thiolate anion of intermediate (**6**) as shown in Scheme 2. This novel method for the preparation of cyclic trithiocarbonates has a great advantage from the point of synthetic convenient and utility.

Experimental

All melting points were uncorrected. IR spectra were obtained on a Jasco IR-G spectrophotometer and NMR spectra

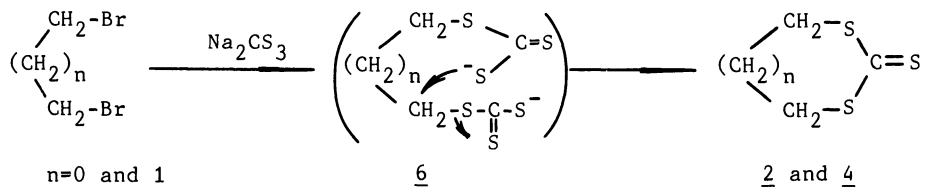


Scheme 1.

Table 2. Synthesis of 1,3-Dithiane-2-thiones **4** from Substituted 1,3-Dibromopropane with Na_2CS_3 in the Presence of PTC

Run[a]	Substrate **3**			React		Yield of **4**/%[b]	
	R^1	R^2	X	Temp/°C	Time/h		
1[c]	H	H	Br	60	1	7	**4a**
2	H	H	Br	60	1	38	**4a**
3[d]	H	H	SH	100	3	45	**4a**
4	CH_3	H	Br	rt	1	23	**4b**
5[c]	CH_3	H	Br	60	1	17	**4b**
6	CH_3	H	Br	60	1	60	**4b**
7	CH_3	H	Br	60	5	66	**4b**
8	CH_3	CH_3	Br	60	20	31	**4c**

a) 1,3-Dibromopropane, 2 mmol; Na_2CS_3, 6 mmol; TOMAC, 0.08 mmol. b) Isolated yield based on substrate **3**. c) Absence of TOMAC. b) 1,3-Propanedithiol, 2 mmol; CS_2, 6 mmol; NaOH, 2.5 mmol.



Scheme 2.

were measured with a Varian Gemine-200 spectrophotometer (200 MHz) in $CDCl_3$ using TMS as in internal standerd. Elemental analyses were determined with a Yanagimoto MT-3.

General Procedure. To a solution of 1,2-dibromoethane (2 mmol) in benzene (5 ml) were added Na_2CS_3 30% aqueous solution (6 mmol) and trioctylmethylammonium chloride (0.08 mmol); then, the mixture was heated with stirring at 60 °C for 8 h. After completion of the reaction, the benzene layer was washed with water and then dried on sodium sulfate. A yellow oil obtained by the evaporation of benzene was chromatographed on silica gel using dichloromethane–hexane (3:1) as an eluent to give the desired 1,3-dithiolane-2-thione (**2a**) in a yield of 97%. The structures of the products were characterized by ^1H NMR, IR, MS, and elemental analyses. The physical and spectral data of thione **2a**, **4a**, and **4b** were identified with those of authentic samples.[2,9,10]

4-Methyl-1,3-dithiolane-2-thione (2b): Oil; IR (neat) 1032, 1048, and 1077 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.65 (d, 3H, J=6,6 Hz, CH_3), 3.70 (q, 1H, J=11.8, 7.4 Hz, CH), 4.04 (q, 1H, 7.4, 5.7 Hz, CH), and 4.55 (m, 1H, J=11.8, 6.6, and 5.7 Hz, CH). Found ; C, 32.19; H, 4.09%. Calcd for $C_4H_6S_3$: C, 31.96; H, 4.02%.

4-Ethyl-1,3-dithiolane-2-thione (2c): Oil; IR (neat) 1048 and 1088 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.09 (t, 3H, J=7.4 Hz, CH_3), 1.99 (m, 2H, CH_2), 3.72 (q, 1H, J=12.0, 7.6 Hz, CH), 4.00 (q, 1H, J=12.0, 5.6 Hz, CH), and 4.34 (m, 1H, CH). Found: C, 36.70; H, 4.97%. Calcd for $C_5H_8S_3$: C, 36.54; H, 4.91%.

4,5-Dimethyl-1,3-dithiolane-2-thione (2d): Oil; IR (neat) 1050, 1065, and 1090 cm^{-1}; ^1H NMR ($CDCl_3$) (mixture of cis and trans) δ=1.52, 1.60 (d, 6H, CH_3) and 4.10, 4.50 (m, 2H, CH). Found: C, 36.69; H, 4.66%. Calcd for $C_3H_8S_3$: C, 36.54; H, 4.91%.

4,6-Dimethyl-1,3-dithiane-2-thione (4c): Oil; IR (neat) 930, 990, and 998 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.46 (d, 6H, J=7.0 Hz, CH_3), 2.19 (t, 2H, J=6.0 Hz, CH_2), and 3.64 (m, 2H, J=7.0, 6.0 Hz, CH_2). Found: C, 40.65; H, 5.76%. Calcd for $C_6H_{10}S_3$; C, 40.40; H, 5.63%.

4-Mercaptomethyl-1,3-dithiolane-2-thione (5): Oil; IR (neat) 2500 and 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77 (t, 1H, J=9.0 Hz, SH), 3.05 (m, 2H, CH_2), 3.99 (q, 1H, J=12.2, 4.4 Hz, CH), 4.19 (q, 1H, J=12.2, 5.4 Hz, CH), and 4.36 (m, 1H, CH). Found: C, 26.45; H, 3.32%. Calcd for $C_4H_6S_4$: C, 26.34; H, 3.32%.

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