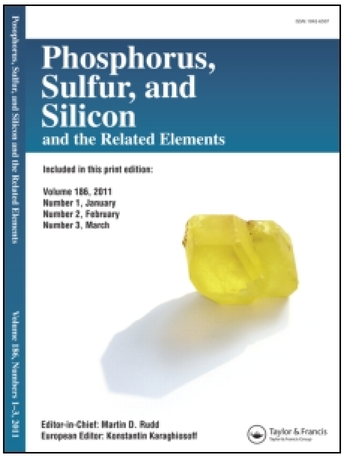

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CONVERSION OF CYCLIC TRITHIOCARBONATES TO THIOACETALS, INCLUDING 1,3-DITHIANE, BY REDUCTION WITH DIISOBUTYLALUMINIUM HYDRIDE (DIBAL)

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Cyclic trithiocarbonates can be desulfurized with diisobutylaluminium hydride (DIBAL) to form the corresponding thioacetals. This new synthetic pathway was exploited for the preparation of several Umpolung reagents, including 1,3-dithiane. An efficient isolation of sodium trithiocarbonate is described.

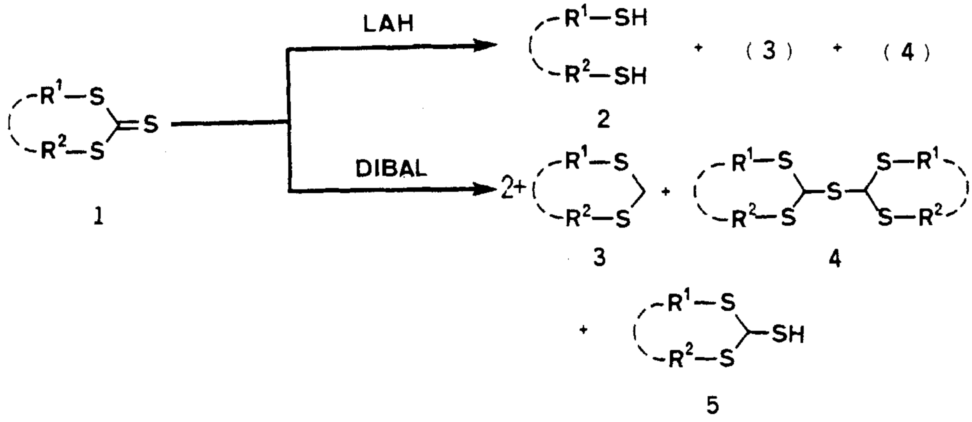
INTRODUCTION

We have studied the behaviour of various hydride reagents towards cyclic and acyclic trithiocarbonates. While it is known that lithium aluminium hydride (LAH) reacts with cyclic trithiocarbonates to give ring fission,[1] we found that with diisobutylaluminium hydride (DIBAL), dithioacetals are the main products, as depicted in Scheme 1.

The trithiocarbonates were obtained by several routes. (1) The 1,3-dipolar cycloaddition of carbon disulfide to the sulfur ylide, thermally generated from 1,2,3-benzothiadiazole,[2] proves to be an efficient method for the synthesis of **1a**. *CAUTION*: The need for a steam distillation in the preparation of 1,2,3-benzothiadiazole is not mentioned explicitly in the original.[2a] An attempt to use an extractive workup of the reaction mixture followed by an ordinary distillation resulted in violent decomposition. Several runs were carried out safely using the procedure outlined in the Experimental Section. The alternative preparation of **1a**, i.e. cyclization of **2a** (obtained from 1,2-dibromobenzene by a published route[3]) to **1a** with thiophosgene, was less attractive for economic reasons. (2) **1b** was purchased. (3) For the preparation of cycloaliphatic trithiocarbonates, either dithiols[4,5] or dihalides and the corresponding mesylates[5d] are the usual starting materials.[5] Since the dithiols are prepared routinely from the dihalides[6] and have noxious odors, we preferred to introduce the CS_3 functionality via sodium trithiocarbonate. We were surprised to find that no efficient procedure for the preparation of this salt existed, most authors choosing to use it *in situ*.[7] We report the optimized isolation of Na_2CS_3 and its use for the preparation of **1c**. (4) **1d** and **1e** were prepared as previously described.[4b]

RESULTS

The results of the reductions of these trithiocarbonates are shown in Table I. At reflux temperature, the sole product from reduction of **1a** with LAH is **2a**, while at room temperature, a mixture of **2a**, **3a**, and **4a** is formed. With DIBAL, the yields of



compound	R^1, R^2
1a, 2a, 3a, 4a	*o*-phenylene
1b, 2b, 3b	$—(CH_2)_2—$
1c, 2c, 3c, 4c, 5c	$—(CH_2)_3—$
1d, 2d	phenyl
1e, 2e	benzyl

SCHEME 1

TABLE I

Reduction of trithiocarbonates

Substrate	Hydride reagent	Temp., °C	Products, % **2**	Products, % **3**	Yield[a] **4**	Yield[a] **5**
1a	LAH	ref. 1b	b			
		110	60[c]	0[d]		
		20	16[e]	35	11	
	DIBAL	0		60		
		110		88[f]		
1b	LAH	ref. 1c	86			
	DIBAL	110		59[c]		
1c	LAH	ref. 1c	37			
	DIBAL	−70			g	50
		−18	8[h]	11		8[h]
		−10	g	21	8	
		20		26[c]		
		110		67[f]		
1d	DIBAL	−70	73[i]	0[d]		
		0	85[h]	0[d]		
		110	95[h]	0[d]		
1e	DIBAL	110	86[h]			

[a] Isolated yield of pure products. See also Table II.
[b] No yield cited.
[c] Yield not optimized.
[d] No product **3** detectable on TLC.
[e] Isolated as dithioveratrole.
[f] Optimized yield from several runs.
[g] Small amount seen on TLC.
[h] Isolated as *S*-benzyl derivative.
[i] Isolated as thioanisole.

TABLE II

Products of the reduction reactions

Product	Purification	mp (°C) or bp (mbar)	^{1}H NMR, δ (integration, splitting)
2a	acidification of NaOH phase, extraction and Kugelrohr distillation	60[a], 0.03	3.65 (2 H, s[b]), 7.05 (4 H, m)
4a	flash chromatography, petroleum ether as eluent	143 (lit.[8] 145–7)	6.14 (2 H, s), 7.20 (8 H, m); 57.7, 123.2, 126.1, 136.0[c]
3a	distillation	80, 0.05 (lit.[15] 88, 0.06)	d
5c	same as **2a**	80, 0.02	2.10 (2 H, m), 2.75 (1 H, s)[b], 3.10 (4 H, m), 5.21 (1 H, d)
4c	recrystallization of unsublimable residue from **3c** from CH_2Cl_2 and petroleum ether	158–160	2.40 (4 H, m), 3.30 (8 H, m), 4.92 (2 H, s)
3c	sublimation as described in lit.[12]	54–55 (lit.[12] 53–54)	2.10 (2 H, m), 2.85 (4 H, t) 3.80 (2 H, s)
2d[f]	workup of alkaline phase after alkylation with benzyl chloride	115, 0.01[f]	e
2e[g]	same as **2d**	130, 0.02[g]	3.50 (4 H, s), 7.15 (10 H, s)

[a] Temperature of air bath.
[b] Exchangeable with D_2O after addition of trace amount of CF_3CO_2H.
[c] ^{13}C NMR, ppm.
[d] ^{1}H NMR is identical with lit.[9,15]
[e] ^{1}H NMR is identical with lit.[16]
[f] Phenylbenzylsulfide.
[g] Dibenzylsulfide.

3a and **3c** are increased at higher temperatures. Because **3c** is stable to an excess of DIBAL at 110°, it cannot be an intermediate in the formation of **2c**.

The physical properties of the reduction products are summarized in Table II. Bis(1,3-benzodithiol-2-yl)sulfide (**4a**) has been prepared before[8] by reduction of 2-(3-methylbutoxy)-1,3-benzodithiole with hydrogen sulfide, but the corresponding **4c** is new. The structure of **4c** was determined by ^{1}H NMR, mass spectroscopy, and microanalysis, and the compound was found to have physical properties analogous to those for similar compounds.[9] In particular, the relative intensity of the molecular ion peak of **4c** is very low (4.9%), with the $C_4H_7S_2^+$ fragment (m/e = 119) predominating (100%). The observed M + 1 and M + 2 peak intensities agree with the calculated[10] values for $C_8H_{14}S_5$.

DISCUSSION

We are currently investigating the mechanism of the formation of products **4** as well as the different behavior of the acyclic trithiocarbonates **1d** and **1e**, which form fission products **2d** and **2e** exclusively. We are also exploring the scope and limitations of this reaction by examining the behavior of the trithiocarbonates with other hydride reagents.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained either on a Perkin Elmer R12A (60 MHz) or JEOL FX-90Q (90 MHz) spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra (MS) were obtained on a VARIAN MAT SM1 B instrument at 70 eV. Ethylene trithiocarbonate (**1b**) was purchased from Aldrich. The hydride reagents were lithium aluminium hydride (LAH) from Merck-Schuchardt and diisobutylaluminium hydride (DIBAL) (25% solution in toluene) from Aldrich. Toluene (Merck "reinst") was distilled and stored over sodium wire. All glassware was dried thoroughly in a drying oven and cooled under a stream of dry nitrogen. Reduction experiments were carried out under a dry nitrogen (or dry argon atmosphere for small scale runs) and hypodermic syringes were used to transfer hydride solutions.[11] The concentration of DIBAL solution was determined according to Crompton[14] using purified N-methylaniline and a simplified mercury-filled gas burette.[11] Flash chromatography was performed on silica gel (Merck Kieselgel 60 0.043–0.060 mm).

Sodium trithiocarbonate. A solution of sodium isopropoxide in 500 mL dry isopropanol (99.8% Merck), prepared from sodium metal (30.0 g, 1.3 gAt) by reflux, was saturated at room temperature with a stream of dry ($CaCl_2$-tower) hydrogen sulfide under stirring with the formation of a white precipitate of sodium bisulfide. Freshly distilled carbon disulfide (61.0 g, 0.8 mol) was added and the heterogenous, yellow reaction mixture was refluxed for three hours. Addition of dry ether (100 mL) to complete precipitation, filtration, and washing (3 × 50 mL ether) produced sodium trithiocarbonate as a yellow salt, which was dried over potassium hydroxide in vacuo: yield 95.2 g (95%). The product was stored in the refrigerator and handled with minimum exposure to moisture.

1,3-Dithiane-2-thione (**1c**). To a suspension of Na_2CS_3 (7.70 g, 50 mmol) in ethanol (200 mL) was added a solution of 1,3-dibromopropane (10.1 g, 50 mmol) in ethanol (50 mL) at reflux temperature. Heating was continued for three hours. Dilution with water (400 mL) and extraction with methylene chloride produced, after drying (Na_2SO_4) and evaporation of the solvent, a crystalline product, that was recrystallized from methanol: 5.4 g (72%), mp 78–79° (lit.[4c,5d–f] 79°,80°) ^1H NMR identical with lit.[5e] When isopropanol was used instead of ethanol, the yield was 65%.

1,2,3-Benzothiadiazole. 2-Aminothiophenole (62.5 g, tech. grade, 90%, Aldrich, ca. 0.45 mol) and a solution of $NaNO_2$ (35.4 g, 0.5 mol) in 60 mL water were added at a uniform rate at 15–20° to 400 mL stirred acetic acid. Stirring was continued until the green color changed to red (30–40 min). Steam distillation (see *CAUTION* on page 1!) produced 4 L distillate which was extracted with methylene chloride (500 mL and 2 × 200 mL). The combined extracts were washed with 5% $NaHCO_3$, dried ($CaCl_2$) and evaporated to produce 55.5 g of a crude product which was distilled. The fraction boiling from 108–114°/10 mmHg amounted to 45.9 g (75%).

1,3-Benzodithiole-2-thione (**1a**). Compound **1a** was prepared in 56–68% yield according to lit.[2a] (recrystallized from toluene) mp 165–166° (lit.[2a] 164°).

General procedure for the reduction of trithiocarbonates. To the yellow solution (or partial suspension at low temperatures) of **1** (10 mmol) in dry toluene (20 mL), DIBAL (1.48 M in toluene, 13.5 mL) was added slowly resulting in discoloration. The progress of the reaction was followed by TLC utilizing molybdatophosphoric acid (10% in ethanol) and palladium chloride (0.5%) for visualization. The reaction mixture was poured, with stirring, into a 1 : 1 mixture of crushed ice and 40% NaOH (100 mL).[13] Extraction with ether (3 × 50 mL), washing of the ether phase with 2N NaOH, and drying (Na_2SO_4 or $MgSO_4$) produced, after evaporation of the solvent, the crude product, which was further purified as indicated in Table II. The combined NaOH phases were stirred with excess methyl iodide or benzyl chloride overnight and extracted with methylene chloride.

Reductions with LAH were performed analogously, employing solutions of LAH in ether or THF prepared, and were analyzed according to the lit.[11]

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