Synthesis of 5,5-Disubstituted-1,2,3-trithianes.

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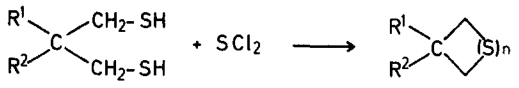
5,5-Disubstituted-1,2,3-trithianes have been prepared by heating an alcoholic sodium tetrasulfide solution with 2,2-dimethyl-1,3-dibromopropane[2]. By-products formed were: 4,4-dimethyl-1,2-dithiolane and 3,3-dimethyl-thietane, probably due to some dismutation of the tetrasulfide on heating. Two alternatives for the synthesis of the title compounds are possible. Method A consists of reacting a 1,3-dithiol with sulfur dichloride at low temperature in a volatile solvent. Here too, the reaction mixture contains the corresponding 1,2-dithiolane (Scheme A).



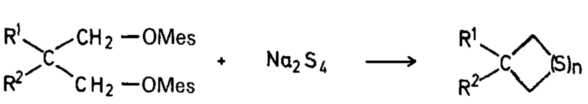
1 **2** **3** n=2,3

$R^1 = R^2 = C_2H_5$;

$R^1 - R^2 = -(CH_2)_4-$, $-(CH_2)_5-$;

$R^1 = CH_3$, $R^2 = C_2H_5$, $n-C_3H_7$, $i-C_3H_7$, $s-C_4H_9$

Scheme A



4 **5** **3** n=2,3

$R^1 = R^2 = CH_3, C_2H_5, i-C_4H_9$

$R^1 = CH_3$, $R^2 = neo-C_5H_{11}, C_6H_5, i-C_4H_9$

Scheme B

Heating of a dimesylate with sodium tetrasulfide (Scheme **B**) results also in a mixture of cyclic di- and trisulfide. The amount of the former is limited if the solvent, after extraction, is distilled off at atmospheric pressure rather than in vacuo; and the ratio trithiane/dithiolane, determined by ^{1}H-N.M.R.-spectroscopy, is almost better than 2:1.

Table. Preparation of 5,5-Dialkyl-1,2,3-trithianes

R^1	R^2	Method	Conversion (%)	Yield (%)	S-analysis calc.	S-analysis found
CH_3	CH_3	B	68	79	57.03	57.29
C_2H_5	C_2H_5	A	63	75	49.48	49.10
		B	65	70		49.05
i-C_4H_9	i-C_4H_9	B	60	55	38.40	38.55
$-(CH_2)_4-$		A	65	68	50.00	50.09
$-(CH_2)_5-$		A	70	65	46.60	46.23
CH_3	C_2H_5	A	67	72	53.33	53.39
CH_3	n-C_3H_7	A	67	69	49.48	49.73
CH_3	i-C_3H_7	A	60	58	49.48	49.61
CH_3	s-C_4H_9	A	59	57	46.15	46.01
CH_3	i-C_4H_9	B	65	74	46.15	46.10
CH_3	neo-C_5H_{11}	B	63	62	43.24	43.57
CH_3	C_6H_5	B	55	49	42.10	42.19

All synthesised 1,2,3-trithianes (see Table) were isolated by preparative G. L. C. (SE 30)[6] and identified by M. S. (molecular ion peak and others corresponding to M—S, M—HS_2, M—HS_3), U.V. ($\lambda_m \sim 265$ nm, independant of the solvent or the nature of the R^1,R^2-groups) and ^{1}H-N.M.R.-spectroscopy (100 MHz). Sulfur analyses were based on the Schöniger combustion-method[3].

As both 1,2-dithiolanes and 1,2,3-trithianes can be smoothly reduced to 1,3-dithiols by sodium in liquid ammonia[2,4] and as dimesylates can be generated in good yield from the corresponding diols[5], it is clear that Method **B** may be a very promising intermediate in the conversion diol→dithiol.

Preparation of 1,2,3-Trithianes; General Procedure:

Method A: Two solutions, one of freshly distilled sulfur dichloride (0.05 mol) in dry n-pentane (50 ml) and one of the dithiol (0.05 mol) and dry triethylamine (0.1 mol) in dry n-pentane (50 ml), are added slowly together to n-pentane (240 ml), at $-75°$ to $-85°$ (nitrogen atmosphere, and rapid stirring). After the addition is completed, the mixture is allowed to warm to room temperature. After washing with cold water, the solution is dried (Na_2SO_4).

Method B: Sodium sulfide nonahydrate (0.125 mol) is dissolved in water (45 ml), sulfur (0.375 g-atom) is added, and the mixture heated until a clear, dark red, solution results.

A sample (9 ml) of this solution is added to a mixture of a dimesylate (0.125 mol) in hexamethylphosphoric triamide (300 ml). The reaction mixture is heated to 100° for 4 hours and during the first two hours the remaining sodium tetrasulfide-solution is added dropwise. After cooling, the mixture is extracted with n-pentane. The extract is dried (Na_2SO_4) and the solvent is distilled of.

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[1] Aspirant of the N.F.W.O.

[2] H. J. Backer, A. F. Tamsma, *Rec. Trav. Chim. Pays-Bas* **57**, 1183 (1938).

[3] J. M. Dominicus, J. L. Wagemans, *Mededelingen V. C. V.* **1968**, 194.

[4] H. J. Backer, N. Evenhuis, *Rec. Trav. Chim. Pays-Bas* **56**, 129 (1937); **56**, 174 (1937).

[5] L. Fieser, M. Fieser, *Reagents for Organic Synthesis*, John Wiley and Sons, Inc., New York, 1967, p. 662.

[6] G. L. C. separation: because of possible reduction of tri- to disulfides, the contact between products and metal at high temperatures was minimised by inserting a glass tube in the injector, using all glass columns and placing a by-pass between column and detector.