

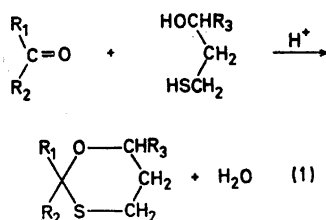
Properties and Reactions of 1,3-Oxathianes

I. Preparation of 1,3-Oxathiane and Its 2- and 6-Alkyl Derivatives

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As their symmetrical analogs, the 1,3-dioxanes¹⁻⁴ and 1,3-dithianes,⁵ had recently been extensively studied, 1,3-oxathianes were considered very interesting objects for conformational and kinetic investigations. As a continuation of our series of papers dealing with aliphatic heterocycles,^{1-4,6-8} this paper reports the preparation of 1,3-oxathiane and several of its 2- and 6-alkyl derivatives:



$R_1 = H$ or Me; $R_2 = Me, Et, Pr^i,$ or $t-Bu$;
 $R_3 = H$ or Me

3-Mercaptopropanol was prepared from 3-chloropropanol (Fluka AG) and thiourea (Fluka AG) by the method of Clinton *et al.*⁹ (Table 1). 1-Methyl-3-mercaptopropanol was prepared from thiourea and 3-chloro-1-methylpropanol and 3-chloro-3-methylpropanol by

the same method. The isomeric chloroalkanols were not separated since thiourea was found to react predominantly with the primary halide. The yield of 1-methyl-3-mercaptopropanol was only about 25 %, but as the mixture of chloroalkanols contained only 63 % of the primary halide, the actual yield was about 40 % (Table 1).

The mixture of the above chlorobutanols was prepared by methanolysis of a 63:37 mixture of the primary and secondary esters formed when 1,3-butanediol (Fluka AG) reacted with acetyl chloride.^{10,11}

1,3-Oxathiane and its derivatives were prepared from 3-mercaptopropanol or 1-methyl-3-mercaptopropanol and the appropriate aldehyde or ketone by the following general method:

A mixture consisting of 0.1 mole of mercaptoalkanol, 0.11 mole of the aldehyde or ketone, 0.1 g of *p*-toluenesulfonic acid, and 50 ml of dichloromethane was boiled in a water entrainment unit until the formation of water ceased. The solution was neutralized with diethylamine and filtered. The dichloromethane was removed by distillation and the residue was fractionated at reduced pressure.

Physical constants of the prepared 1,3-oxathianes are shown in Table 2.

Aldehydes were found to react with the mercaptoalkanols rapidly (1–2 h) and the yields were very satisfactory (60–70 %) except that formaldehyde gave 1,3-oxathiane in only 20 % yield. Acetone was the most reactive ketone, whereas *t*-butyl methyl ketone reacted very slowly (after 5 days, the yield of acetal was 30–35 %).

The purities of the prepared compounds were checked with a Perkin-Elmer F 11 gas chromatograph equipped with a column containing 5 % Carbowax 20 M on Chromosorb W (60/80 mesh). Most of the synthesized compounds were run through a Perkin-Elmer F 21 preparative gas chromatograph equipped with a 4.5 m × 3/8 in column containing 5 %

Table 1. Physical constants of the initial reactants.

Compound	B.p., °C/torr	n_D^{20}	d_4^{20}	Yield, %
$CH_3CH(OAc)CH_2CH_2Cl$	60–76/13	1.4277	—	68
$CH_3CHClCH_2CH_2OAc$				
$CH_3CHOHCH_2CH_2Cl$				
$CH_3CHClCH_2CH_2OH$	66–71/15	1.4419	—	65
$HOCH_2CH_2CH_2SH$	69–72/10	1.4962	1.0650	43
$CH_3CHOHCH_2CH_2SH$	82–85/15	1.4840	1.0166	25

Table 2. Physical constants of the prepared 1,3-oxathianes.

1,3-Oxathiane	B.p., °C/torr	n_D^{20}	d_4^{20}	(R_D)		Yield %
				Obs.	Calc.	
— ^a	48/11	1.5026	1.0867	28.31	28.12	20
6-Me	52–54/13	1.4920	1.0504	32.65	32.74	30
2-Me	66–70/24	1.4922	1.0520	32.61	32.74	77
2-Et	73–75/19	1.4856	1.0090	37.59	37.39	69
2-Pr ⁱ	75–78/16	1.4853	0.9954	42.13	42.07	60
2,2-diMe ^b	65–68/17	1.4890	1.0187	37.46	37.37	65
<i>cis</i> -2,6-diMe	54–56/12	1.4827	1.0109	37.34	37.37	69
<i>cis</i> -2-Et-6-Me	66–69/20	1.4771	0.9803	42.16	42.00	65
<i>cis</i> -2-Pr ⁱ -6-Me	69–72/13	1.4747	0.9682	46.58	46.66	60
2-Et-2-Me	61–63/10	1.4936	1.0139	41.96	42.00	57
2-Pr ⁱ -2-Me	64–67/10	1.4923	0.9987	46.49	46.66	40
2- <i>t</i> -Bu-2-Me	94–97/27	1.4942	0.9846	51.56	51.56	30
2,2,6-triMe	55–57/12	1.4789	0.9879	41.97	41.99	70
2,6-diMe-2-Et ^c	62–64/12	1.4812	0.9791	46.54	46.64	65
<i>trans</i>		1.4804				
<i>cis</i>		1.4827				
2,6-diMe-2-Pr ⁱ (<i>trans</i>)	68–70/12	1.4819	0.9682	51.32	51.31	58
2,6-diMe-2- <i>t</i> -Bu(<i>trans</i>)	68–70/11	1.4827	0.9609	55.95	56.19	35

^a B.p. 67°C/10 torr. n_D^{20} 1.5029 in Ref. 12. ^b B.p. 55–56°C/13 torr, n_D^{20} 1.4888 in Ref. 12.
^c A mixture of stereoisomers.

Carbowax 20 M on Chromosorb G (60/80 mesh). In the case of 2-ethyl-2,4-dimethyl-1,3-oxathiane, the isomeric forms were also separated, but in the case of the other compounds only the *cis* or *trans* form was isolated owing to the great differences in the stabilities.

Also the NMR and mass spectra of the studied 1,3-oxathianes were recorded and found to be consistent with the structures and molecular weights of the compounds, but these will be discussed in a later paper.

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