filtered off, washed with ice water, dried and recrystallized from pentane, m.p. 193°–198°. (Found: C 72.5; H 10.8. Calc. for $C_{26}H_{48}O_4$: C 73.3; H 11.4.) NMR: δ *ca.* 94 and 84 Hz (1:5).

IV. *Procedure a.* To 2.12 g 2-hydroxycyclotridecanone in 25 ml propionic acid were slowly added 5.0 ml 34 % hydrogen peroxide and 2 drops perchloric acid. The reaction mixture was left open to the atmosphere in a fume hood for 4 days at *ca.* 20°. The white residue was washed with ice water, dried and recrystallized twice from chloroform, m.p. 110°–111°. (Found: C 63.4; H 9.6. Calc. for $C_{26}H_{46}O_8$: C 64.2; H 9.5.) IR: absorptions at 3500–2300, 1690 and 915 cm^{-1}. NMR: δ *ca.* 565, 135 and 81 Hz (1:4:9).

Procedure b. 1.05 g cyclotridecane-1,2-dione, 2.5 ml 34 % hydrogen peroxide and 10 ml of propionic acid with 2 drops of percloric acid added, were left for 24 h at *ca.* 20° and treated as in procedure *a*. 1.0 g of a white solid, m.p. 107°–109° resulted. Mixed m.p. with the product from *a* gave no depression.

V. To 2.12 g 2-hydroxycyclotridecanone and 2 drops of perchloric acid was slowly added 1.0 ml 34 % hydrogen peroxide. The mixture was left open to the atmosphere for 24 h at 20°. A white residue was washed with ice water, dried, and washed with small amounts of pentane and benzene, m.p. 77°–82°. (Found: C 63.9; H 10.0. Calc. for $C_{26}H_{48}O_8$: C 64.0; H 9.9.) IR: absorptions at 3600–2300, 1700, and 935 cm^{-1}. NMR: δ *ca.* 585, 381, 148–128, 81 Hz.

A Perkin Elmer 457 Grating Infrared Spectrophotometer and a Varian A 60 A NMR Spectrometer were used.

1. Ružicka, L., Stoll, M. and Schinz, H. *Helv. Chim. Acta* **9** (1926) 249.
2. Stevens, P. G. *J. Am. Chem. Soc.* **67** (1945) 907.
3. Stoll, M. and Rouvé, A. *Helv. Chim. Acta* **30** (1947) 1822.
4. Mori, T., Nakahara, T. and Nozaki, H. *Can. J. Chem.* **47** (1969) 3266.
5. Ledaal, T. and Solbjør, T. *Acta Chem. Scand.* **21** (1967) 1658.
6. Ledaal, T. *Acta Chem. Scand.* **21** (1967) 1656.

Received May 19, 1971.

Properties and Reactions of 1,3-Oxathianes

III. A Novel Route to Alkylated 1,3-Oxathianes

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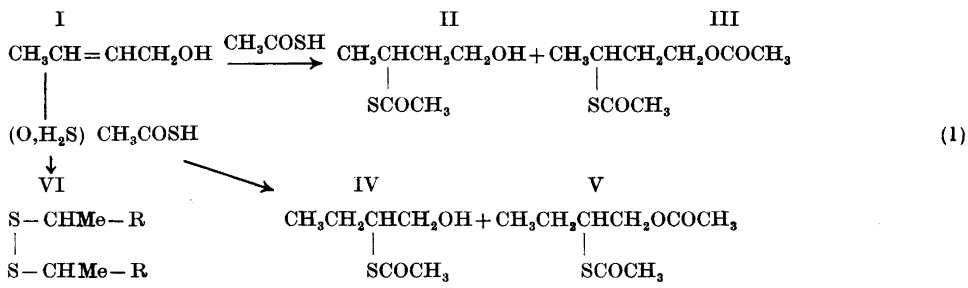
Only a few reports have been published that deal with 1,3-oxathianes, the cyclic acetals of 1,3-hydroxythiols.[1–5] In part I of this series, we reported the preparation of several 2- and 6-alkyl-1,3-oxathianes.[5] In this paper the syntheses of fifteen 1,3-oxathianes methylated at the 2, 4, 5, and 6 position are described.

The synthesis of 1,3-oxathianes has been mostly limited by the shortage of suitable initial reactants. Secondary halides and neopentyl-type halides do not react with thiourea to form products that yield thiols on hydrolysis.[5–7] 3-Mercapto-2,2-dimethyl-1-propanol can, however, be prepared from 3,3-dimethyloxetane and thiourea by the method of Rondestvedt.[7]

It has been shown previously that thioacetic acid adds smoothly to olefins, but that the products formed in the presence of peroxide are "abnormal in character" with respect to Markovnikoffs' rule.[8,9] For this reason, we conducted this addition reaction with the unsaturated alcohols crotyl alcohol, 2-methyl-3-buten-2-ol, 3-methyl-3-buten-2-ol and a mixture of *cis*- and *trans*-3-penten-2-ols.

Crotyl alcohol(I) has been reported to react with thioacetic acid to form 3-acetylthio-1-butanol (II) and the corresponding acetate (III), although the disulfide (VI) is also formed (see scheme (1)).[8,9] However, crotyl alcohol is a "symmetrically" substituted olefin and hence the addition of the two fragments produced on scission of the S–H bond should not take place exclusively at one or the other of the double bond carbons. Consequently, crotyl alcohol should yield a mixture of 1,3- and 1,2-substituted isomers in contrast to the results of Brown *et al.*[8]

Actually, a 2:3 mixture of 3-mercapto-1-butanol and 2-mercapto-1-butanol was obtained after hydrolysis as concluded from the results of gas chromatographic analyses of the product ratios after acetalization. The mixture of *cis*- and *trans*-3-penten-2-



(1)

ols yielded a 7:3 mixture of 1,3- and 1,2-hydroxythiols. The molar ratio of diastereomeric hydroxythiols was about 1:1 in both product components. 3-Methyl-3-buten-2-ol and 2-methyl-3-buten-2-ol are unsymmetrically substituted olefins and the addition of the thioacetate group occurs accordingly only at the 4-carbon atom. 3-Methyl-3-buten-2-ol also yielded nearly equal amounts of the diastereomeric 1,3-hydroxythiols.

General method of addition. A mixture composed of 1 mol of redistilled unsaturated compound (Fluka AG), 2 mol of redistilled thioacetic acid (Fluka AG) and a few drops of ascaridole (Fluka AG) was stirred magnetically overnight. The addition reaction was very sensitive to inhibitors, especially to any free sulfur in the mixture. The exothermic reaction began only when the reactants had been carefully purified.

The alcoholysis of the mixtures of thioacetates was effected by boiling them with 250 ml of methanol that contained 1 ml of conc. hydrochloric acid as catalyst. The products were distilled at reduced pressure.

3-Mercapto-1-butanol was prepared from crotyl alcohol. The boiling range of the addition product was 92–125°/25 mm Hg and the refractive index n_D^{20} 1.4680. The hydrolysis product consisted of 40 % of 3-mercapto-1-butanol and 60 % of 2-mercapto-1-butanol. B.p. 85–95°/15 mmHg, n_D^{20} 1.4750. The yield was 55 %.

4-Mercapto-2-pentanol was prepared from the mixture of *cis-* and *trans*-3-penten-2-ols. The isomeric thioacetates boiled at 70–120°/12 mm and the n_D^{20} of the distillate was 1.4662. The 7:3 mixture of 1,3- and 1,2-isomers isolated after alcoholysis boiled at 73–81°/8 mmHg. n_D^{20} 1.4751. Yield 53 %.

4-Mercapto-2-methyl-2-butanol was prepared from 2-methyl-3-buten-2-ol. The addition product distilled in the range 80–112°/10 mmHg. n_D^{20} 1.4767. The hydroxythiol boiled at 85/20 mm. Yield 86 %.

4-Mercapto-3-methyl-2-butanol was prepared from 3-methyl-3-buten-2-ol. The boiling range of the thioacetates was 75–108°/10 mmHg. and n_D^{20} 1.4812. The approximately equimolar mixture of diastereomeric hydroxythiols isolated after methanolysis boiled at 70–73°/8 mmHg and had n_D^{20} 1.4862. The yield was 87 %.

3-Mercapto-2,2-dimethyl-1-propanol was prepared by the method of Rondestvedt [7] from 3,3-dimethyloxetane and thiourea. B.p. 82–84°/12 mmHg. Yield 50 %.

3,3-Dimethyloxetane was prepared from 2,2-dimethyl-1,3-propanediol by way of the cyclic carbonate.[10] B.p. 78–81°/760 mmHg. n_D^{20} 1.3895. Yield 38 %. (Ref. 10, B.p. 80–81°/760 mmHg; Ref. 11, n_D^{20} 1.3907.)

1,3-Oxathianes were prepared by boiling a mixture of 0.1 mol of a hydroxythiol, 0.11 mol of an aldehyde or a ketone, 0.1 g of *p*-toluenesulfonic acid and 100 ml of methylene chloride in a water entrainment unit. After the theoretical amount of water had been removed, the boiling was continued for half an hour, after which the mixture was neutralized with diethylamine. The solvent was distilled off and the residue fractionated at reduced pressure. 4,6-Dimethyl-1,3-oxathianes were prepared from 4-mercapto-2-pentanol, 4-methyl-1,3-oxathianes from 3-mercapto-1-butanol, 6,6-dimethyl-1,3-oxathianes from 4-mercapto-2-methyl-2-butanol, 5,6-dimethyl-1,3-oxathianes from 4-mercapto-3-methyl-2-butanol and 5,5-dimethyl-1,3-oxathiane from 3-mercapto-2,2-dimethyl-1-propanol. In the first two cases, the isolated 1,3-hydroxythiols contained also 1,2-isomers and the acetalization gave a mixture of 1,3-oxathianes and 4-ethyl-substituted 1,3-oxathiolanes.

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

The purities of the prepared 1,3-oxathianes were checked with a Perkin-Elmer F 11 gas

Table 1. Physical constants and yields of the synthesized 1,3-oxathianes.

1,3-Oxathiane	B.p. °C/torr	n_D^{20}	Yield %
4-Me	50–65/12	1.4903	27
cis-2,4-diMe	65–75/20 [a]	1.4766	81 [a]
trans-2,4-diMe		1.4822	
cis-2-iPr-4-Me	73–85/7	1.4766	80
2,2,4-triMe	60–63/12	1.4768	75
trans-2-Et-2,4-diMe [b]	70–81/18	1.4815	80
cis-2-Et-2,4-diMe [b]			
trans-2-iPr-2,4-diMe [b]	73–85/10	1.4831	82
cis-2-iPr-2,4-diMe [b]			
trans-2-*t*-Bu-2,4-diMe	75–83/8	1.4835	54
cis-4,6-diMe	55–72/10 [a]	1.4826	65 [a]
trans-4,6-diMe		1.4913	
cis-2-*cis*-4-*cis*-6-triMe		1.4726	
cis-2-*trans*-4-*cis*-6-triMe	62–73/8 [a]	1.4814	78 [a]
cis-2-*cis*-4-*trans*-6-triMe		1.4783	
trans-2,2,4,6-tetraMe	59–70/13 [a]	1.4695	78 [a]
cis-2,2,4,6-tetraMe		1.4710	
2,5,5-triMe	70–72/20	1.4763	73
trans-5,6-diMe	54–64/9 [a]	1.4898	62 [a]
cis-5,6-diMe		1.4942	
2,6,6-triMe	68/17	1.4818	75
cis-2-*cis*-5-*cis*-6-triMe [b]		1.4815	
cis-2-*trans*-5-*cis*-6-triMe [b]			
cis-2-*cis*-5-*trans*-6-triMe	54–59/8 [a]	1.4842	85 [a]
cis-2-*trans*-5-*trans*-6-triMe		1.4855	

[a] For a mixture of the isomers.
[b] Not separable with preparative gas chromatograph.

chromatograph equipped with a column containing 5 % Carbowax 20 M on Chromosorb G (60/80 mesh). The 1,3-hydroxythiols were analyzed with a column containing 5 % didecyl phthalate on Chromosorb G (60/80 mesh). Most of the 1,3-oxathianes were run through a Perkin-Elmer F 21 preparative gas chromatograph equipped with a 5 m × 3/8 in column containing 10 % FFAP on Chromosorb A (60/80 mesh) to separate the isomers and any 1,3-oxathiolanes present as impurities. The NMR spectra and the mass spectra [12] of the prepared 1,3-oxathianes were found to be consistent with the structures. The results of the NMR investigations and chemical equilibrations will be published later.

1. Gelan, J. and Anteunis, M. *Bull. Soc. Chim. Belges* **77** (1968) 423.
2. Gelan, J. and Anteunis, M. *Bull Soc. Chim. Belges* **77** (1968) 447.
3. Friebolin, H., Schmid, H. G., Kabuss, S. and Faisst, W. *Org. Magn. Resonance* **1** (1969) 67–86.
4. de Wolf, N. and Buys, H. R. *Tetrahedron Letters* **8** (1970) 551.
5. Pihlaja, K. and Pasanen, P. *Acta Chem. Scand.* **24** (1970) 2257.
6. Frank, R. L. and Smith, P. V. *J. Am. Chem. Soc.* **68** (1946) 2103.
7. Rondestvedt, C. S. *J. Org. Chem.* **26** (1961) 3025.
8. Brown, R., Jones, W. E. and Pinder, A. R. *J. Chem. Soc.* **1951** 2123.
9. Sosnovsky, G. *Free Radical Reactions in Organic Chemistry*, MacMillan, New York 1964.
10. Searles, S., Hummel, D. G., Nukina, S. and Throckmorton, P. E. *J. Am. Chem. Soc.* **82** (1960) 2931.
11. Searles, S., Nickerson, R. G. and Witsiepe, W. K. *J. Org. Chem.* **24** (1959) 1839.
12. Pihlaja, K. and Pasanen, P. *Org. Mass Spectrom.* **5** (1971) 763.

Received June 1, 1971.