

Reflections hkl with $h = 2n + 1$ are markedly weaker than those with $h = 2n$.

The positions of the Hg atoms were derived from the Patterson projections $P(pvw)$ and $P(uvp)$ and the parameter values were refined in a number of least squares cycles using about 1250 reflections ($0kl$, $1kl$, $2kl$, and $4kl$) visually estimated from Weissenberg photographs. $\text{CuK}\alpha$ radiation was used and no absorption corrections were applied. The final R factor was 0.17 and the final parameter values for the 5 Hg atoms in the unit cell (space group $P\bar{1}$) are:

$$\begin{array}{l} 2 \text{ Hg}_1 \text{ in } 2(i) \text{ with } x = 0.8077 (15), \\ y = 0.1767 (6), z = 0.3001 (4), (B = 1.1) \\ 2 \text{ Hg}_2 \text{ in } 2(i) \text{ with } x = 0.3100 (15), \\ y = 0.1793 (6), z = 0.2995 (4), (B = 1.1) \\ 1 \text{ Hg}_3 \text{ in } 1(a) \text{ with } x = 0, \\ y = 0, z = 0, (B = 1.7) \end{array}$$

An electron density map and a difference map calculated with the same limited set of intensity data confirmed the positions and showed that no other Hg atoms were present in the unit cell. The two highest peaks in the difference map (about one tenth of the height of the Hg peaks) occurred at the positions 0.03, 0.28, 0.63 and 0.39, 0.73, 0.03 and probably correspond to the chlorine atoms of the perchlorate groups.

A projection of the structure along the b axis showing the Hg positions, is given in Fig. 1. The shortest Hg-Hg distances are:

$\text{Hg}_1 - \text{Hg}_2$, 3.59 (2) Å and 3.61 (2) Å;
 $\text{Hg}_1 - \text{Hg}_3$, 3.44 (2) Å; $\text{Hg}_2 - \text{Hg}_3$, 3.47 (2) Å
 Other Hg-Hg distances are longer than 5 Å. Thus the structure is built up from infinite one-dimensional complexes running along the a axis of the unit cell.

A comparison with other basic salts of mercury(II) makes it likely that the positions of the bridging oxygens are those marked in Fig. 1, with an oxygen (O_1) at the center of the triangle formed by the three Hg atoms Hg_1 , Hg_2 , and Hg_3 and a hydroxo group, O_2 , joining the two Hg atoms Hg_1 and Hg_2 . This assumption is supported by the presence of peaks at these positions (O_1 : 0.04, 0.19, 0.19) and (O_2 : 0.45, 0.82, 0.60) in the difference map. This arrangement also leads to the expected digonal coordination of the Hg atoms with two linear Hg-O bonds of lengths about 2.0 Å.

The infinite one-dimensional complexes can thus be described as built up from two

infinite $-\text{O}-\text{Hg}-\text{O}-$ chains of the type found in several other structures,^{2,3} joined by additional Hg atoms (Hg_3), or as built up from Hg_3O_3 groups joined by OH bridges (O_2). Alternatively, the complexes can be described as consisting of hexagons with common O-Hg-O edges (Fig. 1). The correct formula should then be $\text{Hg}_5\text{O}_8(\text{OH})_2(\text{ClO}_4)_4(\text{H}_2\text{O})_2$.

Although only the Hg positions have been directly determined in the structure analysis the type of complexes in the crystals seems to be uniquely defined and the structure determination will not be continued further. The structure derived is closely related to those of the other basic perchlorates, which will be reported in separate papers.

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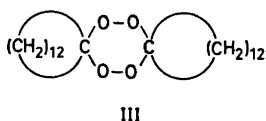
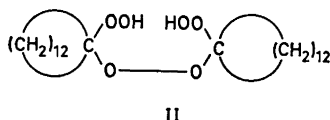
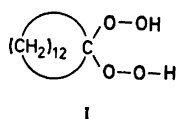
New Cyclotridecane Peroxides

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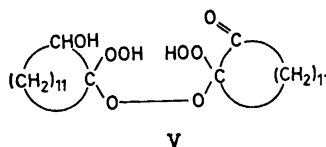
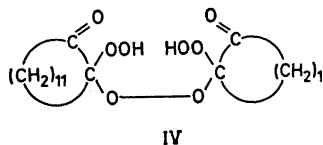
Very few cyclotridecane derivatives are described in the literature,¹⁻⁴ and as far as the present authors are aware, no peroxides are among these. By treating cyclotridecanone, 2-hydroxycyclotridecanone, and cyclotridecane-1,2-dione

with 34 % hydrogen peroxide as previously described,^{5,6} we obtained five different peroxides. Three peroxides, I, II, and III, were isolated from cyclotridecanone. Peroxide I liberates iodine from a solution of sodium iodide in acetonitrile with simultaneous evolution of oxygen. Peroxide II liberates iodine without oxygen evolution, while peroxide III reacts with acidified iodide solution only. Based on chemical tests, spectra and elemental analysis (given in the experimental part) the following structures are proposed for the three peroxides:



By treating 2-hydroxycyclotridecanone or cyclotridecane-1,2-dione with excess hydrogen peroxide a peroxide, IV, was isolated. This reacted slowly and incompletely with neutral as well as with acidic iodide solutions. Another peroxide, V, was obtained by treating 2-hydroxycyclotridecanone with equimolecular amounts of hydrogen peroxide in acetonitrile with a few drops of perchloric acid added. V was less soluble than IV, especially in hydrophobic solvents. It reacted only slowly and incompletely with neutral iodide solutions, more completely, however, in acidic solutions. Iodine was also liberated by grinding the peroxide with dry potassium iodide, which was not the case with peroxide IV. The structures of peroxides IV and V are uncertain. How-

ever, the following, which seem in accordance with elemental analysis and spectra, may be proposed:



The low reactivity towards—and incomplete reaction with—iodide indicate sterically shielded hydroperoxy groups and/or tendency to competing rearrangement reactions.

Experimental. I. 0.98 g cyclotridecanone was dissolved in 5 ml cold formic acid, and 0.5 ml 34 % hydrogen peroxide was slowly added to the stirred and ice cooled solution. Stirring was continued for 20 min after completed addition. A colorless solid was isolated, washed with sodium hydrogen carbonate/ice water and dried *in vacuo* ca. 1.0 g, m.p. 50°–58°. After several washings with pentane was obtained 0.32 g, m.p. 100°–105°. Recrystallization from benzene gave fine needle shaped crystals, m.p. 103°–118° (decomp.). (Found: C 63.5; H 10.4. Calc. for $C_{13}H_{26}O_4$: C 63.4; H 10.6). IR: absorptions at 3200, 1100, 925, and 845 cm^{-1} . NMR: δ ca. 540, 91, and 83 Hz, (ratio 1:2:10).

II. To 0.98 g cyclotridecanone dissolved in 15 ml formic acid was slowly added 1.0 ml hydrogen peroxide. Ca. 0.1 g colorless peroxide, m.p. 128°–129° was isolated. (Found: C 67.3; H 10.6. Calc. for $C_{26}H_{50}O_6$: C 68.1; H 11.0). IR: absorptions at 3360, 1105, 1007, 940, 923, 865, and 817 cm^{-1} . NMR: δ ca. 610, 97, and 84 Hz (1:4:20).

III. 1.96 g cyclotridecanone, 1.0 ml 34 % hydrogen peroxide, 2 drops of 70 % perchloric acid and 10 ml acetonitrile were left open to the atmosphere for 24 h in a fume hood. The residue formed was washed with ice water and dried *in vacuo*. It was then dissolved in propionic acid to which 2 drops of perchloric acid had been added, and the mixture was stirred for 40 min at 0°. A white solid was

filtered off, washed with ice water, dried and recrystallized from pentane, m.p. 193°–198°. (Found: C 72.5; H 10.8. Calc. for $C_{28}H_{48}O_4$: 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 $C_{28}H_{46}O_8$: 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 perchloric 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 $C_{28}H_{48}O_8$: 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.

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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.^{1–3} 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-dimethylloxetane 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-