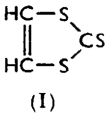
212. *Dithiols. Part XXI.* Dithiols from Cyclic Trithiocarbonates.*

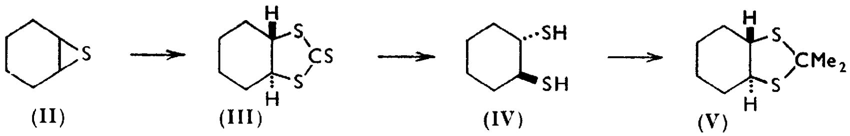
By S. M. IQBAL and L. N. OWEN.

The reductive fission of cyclic trithiocarbonates provides a useful method for the synthesis of dithiols, and is applicable to the preparation of vicinal disecondary thiols which may not be readily accessible by other routes. The method offers particular advantages in the carbohydrate field, and has been used to synthesise three dithiols and one tetrathiol related to the hexitols.

Although cyclopentene oxide does not give a trithiocarbonate with xanthate, cyclopentene sulphide readily gives *trans*-1,2-(thiocarbonyldithio)-cyclopentane (XXX), a compound containing two *trans*-fused five-membered rings. Reasons for this difference in behaviour are discussed.

ALKALINE hydrolysis of cyclic trithiocarbonates is reported [1,2] to give only poor yields of dithiols. It is known, however,[3] that thiols can be prepared very satisfactorily by the reductive fission of xanthates with lithium aluminium hydride, and this procedure should evidently be applicable to trithiocarbonates, though the only report [4] is of the small-scale reduction of the unsaturated cyclic trithiocarbonate (I) to give ethane-1,2-dithiol in unspecified yield.


(I)


(II) (III) (IV) (V)

In some trial experiments, ethane-1,2-, propane-1,3-, propane-1,2-, and cyclohexane-*trans*-1,2-dithiol were obtained by reduction of the corresponding trithiocarbonates with lithium aluminium hydride in yields of 86, 37, 75, and 90%, respectively; for the last two compounds the reported [2] yields by alkaline hydrolysis are 26 and 14%. The configuration of the cyclohexane-*trans*-1,2-dithiol (IV) was not specified by the earlier workers, but since the reductive fission does not affect any asymmetric centre it must be the same as that of the trithiocarbonate (III) from which it is derived; the latter is *trans*, since it is formed through the intermediate episulphide (II).† The dithiol obtained [6] by fission of the episulphide (II) with potassium hydrogen sulphide must also be *trans*. Although cyclohexane-*trans*-1,2-diol does not condense with aldehydes or ketones under normal conditions,[7] the dithiol (IV) readily gave the crystalline isopropylidene derivative (V) on treatment with acetone and a trace of sulphuric acid at room temperature; this is no doubt due to the great stability of the resulting dithiolan system. The corresponding benzylidene and piperonylidene derivatives have already been described,[2] but without comment.

Conventional methods for the synthesis of simple thiols often fail when attempts are made to prepare vicinal dithiols in which both groups are secondary. Thus many vicinal disecondary halides undergo dehalogenation to the olefin, rather than substitution, on

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* Part XX, Fitt and Owen, *J.*, 1957, 2250.

† The mechanism of the formation of cyclic trithiocarbonates is outlined in the preceding paper.[5]

[1] Frassetti, *Ber.*, 1905, **38**, 488.

[2] Culvenor and Davies, *Austral. J. Sci. Res.*, 1948, **1**, *A*, 236.

[3] Djerassi, Gorman, Markley, and Oldenburg, *J. Amer. Chem. Soc.*, 1955, **77**, 568.

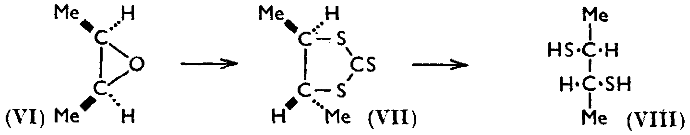
[4] Challenger, Mason, Holdsworth, and Emmott, *J.*, 1953, 292.

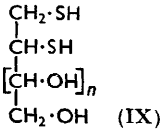
[5] Creighton and Owen, preceding paper.

[6] Culvenor, Davies, and Heath, *J.*, 1949, 282.

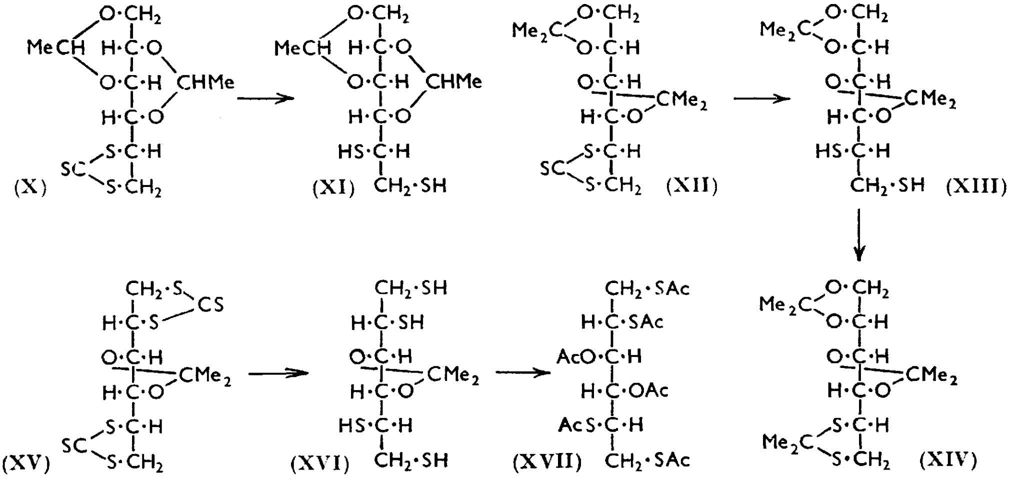
[7] Cf. Christian, Gogek, and Purves, *Canad. J. Chem.*, 1951, **29**, 911.

treatment with sodium hydrogen sulphide, potassium thiolacetate, etc.;[8,9] occasionally,[10] though not always,[9] the difficulty can be surmounted by the use of thiolacetic acid in pyridine, but there is undoubtedly a need for a new method in these difficult cases. The excellent yield obtained in the above preparation of cyclohexane-*trans*-1,2-dithiol indicated that the reduction of a trithiocarbonate should prove particularly useful in this connection, and a further example was provided by the synthesis of DL-*threo*-butane-2,3-dithiol (VIII). Reduction of 3-bromobutan-2-one with potassium borohydride gave the *threo*-bromohydrin, which was converted successively into the *cis*-2,3-epoxide (VI)[11] and the *trans*-trithiocarbonate (VII), which when reduced with lithium aluminium hydride afforded the dithiol (VIII).


(VI) (VII) (VIII)


(IX)

Although αω-dithiols, of known configuration, derived from erythritol, DL-threitol, galactitol, and D-mannitol have been described,[9,12] vicinal dithiols of the type (IX) have been obtained[9,13] only as derivatives of unknown configuration. One pure stereoisomer of 2,3-dimercaptobutane-1,4-diol, and derivatives of both forms, have been prepared,[14] but again the configurations were not established. Since trithiocarbonates related to the carbohydrates are readily made from the appropriate epoxides[5,15] or episulphides[5] such compounds can clearly provide a useful route to polyhydroxy-dithiols. If the trithiocarbonate group engages a terminal position its configuration, and hence that of the resulting dithiol, is unequivocal, though if it is derived from a non-terminal epoxide or episulphide two stereoisomers may be possible. Using this approach we have now obtained three dithiols and one tetrathiol related to the hexitols.


(X) (XI) (XII) (XIII) (XIV) (XV) (XVI) (XVII)

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[8] Rosenheim and Stadler, *Ber.*, 1905, **38**, 2687; Danielli, Danielli, Fraser, Mitchell, Owen, and Shaw, *Biochem. J.*, 1947, **41**, 325; Gavrilov and Tishchenko, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 1687; Pavlic, Lazier, and Signaigo, *J. Org. Chem.*, 1949, **14**, 59.

[9] Evans, Fraser, and Owen, *J.*, 1949, 248.

[10] Pavlic, U.S.P. 2,408,094/1946.

[11] Winstein and Lucas, *J. Amer. Chem. Soc.*, 1939, **61**, 1576.

[12] Bladon and Owen, *J.*, 1950, 585.

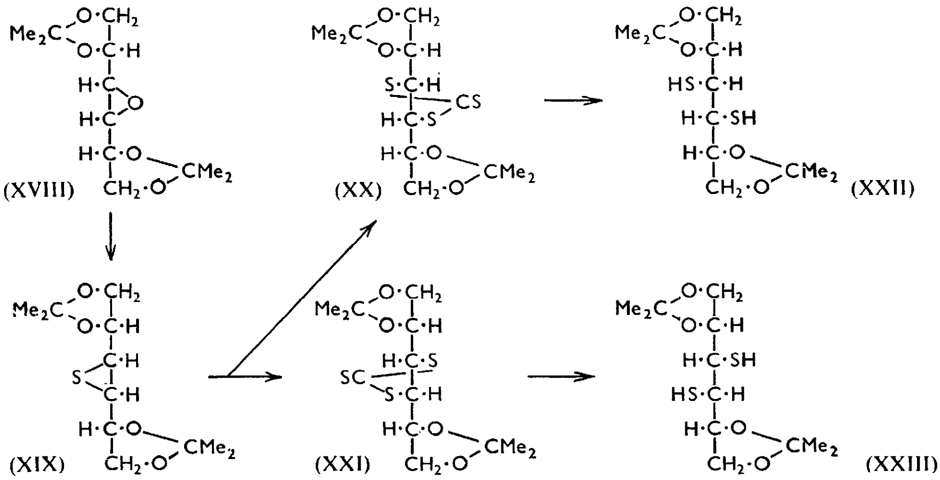
[13] Bladon and Owen, *J.*, 1950, 598.

[14] Fitt and Owen, *J.*, 1957, 2240.

[15] McSweeney and Wiggins, *Nature*, 1951, **168**, 874.

Reduction of 5,6-dideoxy-1,3:2,4-di-*O*-ethylidene-5,6-(thiocarbonyldithio)-L-iditol (X)[5] with lithium aluminium hydride gave an excellent yield of crystalline 5,6-dideoxy-1,3:2,4-di-*O*-ethylidene-5,6-dimercapto-L-iditol (XI). Similar treatment of 5,6-dideoxy-1,2:3,4-di-*O*-isopropylidene-5,6-(thiocarbonyldithio)-L-gulitol (XII)[5] gave 5,6-dideoxy-1,2:3,4-di-*O*-isopropylidene-5,6-dimercapto-L-gulitol (XIII) as a liquid, which readily afforded the crystalline tri-isopropylidene compound (XIV). Reaction of 1,2:5,6-di-anhydro-3,4-*O*-isopropylidene-D-mannitol[16] with potassium methyl xanthate gave 1,2,5,6-tetradeoxy-3,4-*O*-isopropylidene-1,2:5,6-di(thiocarbonyldithio)-L-iditol (XV), from which the liquid tetrathiol, 1,2,5,6-tetradeoxy-3,4-*O*-isopropylidene-1,2,5,6-tetramercapto-L-iditol (XVI) (characterised as the tetra-*S*-acetyl derivative) was obtained in good yield; hydrolysis, followed by acetylation, gave the crystalline hexa-acetyl compound (XVII).

The non-terminal epoxide, 3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-D-talitol (= -D-altritol) (XVIII), which is known[17] to be much less reactive than a terminal epoxide, reacted slowly with xanthate to give a trithiocarbonate which appeared to be homogeneous and which on reduction gave a crystalline dithiol. The intermediate episulphide (XIX) (which in this instance clearly has the same configuration as the epoxide) could give the two trithiocarbonates (XX) and (XXI), and consequently the dithiol has either the D-mannitol (XXII) or the D-iditol configuration (XXIII).



Treatment of cyclopentene oxide (XXV) with potassium methyl xanthate gave *trans*-2-mercaptocyclopentanol as the only recognisable product, but when cyclopentene sulphide (XXVIII) was used in place of the epoxide the trithiocarbonate (XXX) was obtained in good yield. The failure to obtain the trithiocarbonate from the epoxide must therefore be due to non-formation of the episulphide. It is known that cyclopentene oxide, unlike cyclohexene oxide, cannot be converted into the episulphide by reaction with thiourea[18] or thiocyanate,[19] and this has been attributed to the fact that the necessary intermediate (*e.g.* XXIV), containing two *trans*-fused five-membered rings, would be highly strained and consequently not formed. A similar explanation is applicable to the present case, in which attack by the anionic oxygen in the ester (XXVI) on the thiocarbonyl carbon atom, which would give the required intermediate (XXVII), evidently does not occur. The formation of the trithiocarbonate (XXX), which itself contains precisely this type of strained system, involves an attack (cf. XXIX) which is identical with that in the ester

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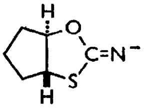
[16] Wiggins, *J.*, 1946, 384.

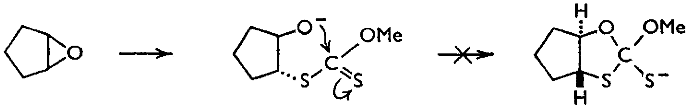
[17] Bladon and Owen, *J.*, 1950, 604.

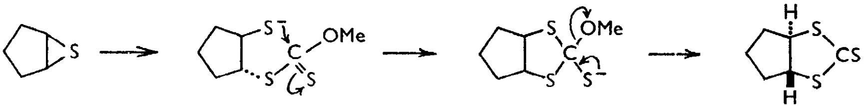
[18] Bordwell and Andersen, *J. Amer. Chem. Soc.*, 1953, **75**, 4959.

[19] van Tamelen, *J. Amer. Chem. Soc.*, 1951, **73**, 3444.

(XXVI) except that it involves a thiol anion instead of the oxygen anion. This striking difference in behaviour can probably be attributed mainly to the much greater nucleophilic reactivity of the thiol anion,[20] but ring closure may also be facilitated by an enhanced ease of deformation of bond angles when oxygen is replaced by sulphur.


(XXIV)


(XXV) (XXVI) (XXVII)


(XXVIII) (XXIX) (XXX)

A trithiocarbonate could not be obtained from either trimethylene oxide or trimethylene sulphide by treatment with xanthate, even under drastic conditions; the greater stability of the four- compared with the three-membered ring system is of course well known.

The C=S stretching frequency in the infrared region is dependent upon the molecular environment of the group. Whilst simple acyclic trithiocarbonates show absorption[21] at 1058—1053 cm.$^{-1}$, ethylene trithiocarbonate is reported by Haszeldine and Kidd[22] to absorb at 1078 cm.$^{-1}$ and by Jones, Kynaston, and Hales[23] at 1074 cm.$^{-1}$. With the exceptions of (VII) and (XXX), all our cyclic trithiocarbonates, including the six-membered trimethylene trithiocarbonate, showed a band in the range 1081—1071 cm.$^{-1}$; most of the compounds exhibited multiple high-intensity maxima near this region (see Table).

Infrared absorption maxima (in carbon tetrachloride) in the range 1125—1000 cm.$^{-1}$.

Trithiocarbonate	$\nu_{\text{max.}}$ (cm.$^{-1}$)	*Trithiocarbonate*	$\nu_{\text{max.}}$ (cm.$^{-1}$)
Ethylene	1081	(X)	1117, 1095, 1081, 1046
Propylene	1081, 1058, 1036		
Trimethylene	1081, 1033	(XII)	1074
Cyclohexene (III)	1106, 1081, 1068, 1052	(XV)	1081, 1071
		(XX) or (XXI)	1074
threo-But-2-ene (VII)	1093, 1058	*trans*-Cyclopentene (XXX)	1099, 1062

EXPERIMENTAL

Microanalyses were by Miss J. Cuckney and the staff of the Organic Chemistry Microanalytical Laboratories, and infrared spectra (recorded in carbon tetrachloride) by Mr. R. L. Erskine, B.Sc., A.R.C.S., and Mrs. A. I. Boston.

Optical rotations were measured in chloroform.

General Method of Reduction of Trithiocarbonates.—The trithiocarbonate in anhydrous ether or anhydrous tetrahydrofuran was added dropwise during *ca.* 30 min. to a stirred slurry of lithium aluminium hydride in anhydrous ether at a rate such that the yellow colour was continuously discharged; the heat of reaction was sufficient to cause gentle refluxing. The mixture was then cooled to 0°, cautiously treated with water to decompose excess of hydride, then acidified with ice-cold 6N-hydrochloric acid and immediately extracted with ether. The extracts were washed with sodium hydrogen carbonate solution, dried ($MgSO_4$ or Na_2SO_4), and concentrated under reduced pressure.

Ethane-1,2-*dithiol.*—2-Thio-1,3-dithiolan[24] (20 g.) in tetrahydrofuran (100 c.c.) was reduced with lithium aluminium hydride (9 g.) in ether (75 c.c.) to give ethane-1,2-dithiol (12 g., 86%), b. p. 68—70°/24 mm., n_D^{20} 1·5582 (Found: thiol-S, 66·7. Calc. for $C_2H_6S_2$: thiol-S, 68·2%).

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[20] Cf. Quale and Royals, *J. Amer. Chem. Soc.*, 1942, **64**, 226; de la Mare and Vernon, *J.*, 1956, 41.
[21] Mecke, Mecke, and Lüttringhaus, *Z. Naturforsch.*, 1955, **105**, *B*, 367.
[22] Haszeldine and Kidd, *J.*, 1955, 2901.
[23] Jones, Kynaston, and Hales, *J.*, 1957, 614.
[24] Culvenor, Davies, and Pausacker, *J.*, 1946, 1050.

Propane-1,2-*dithiol*.—4-Methyl-2-thio-1,3-dithiolan [2] (11·5 g.) in ether (75 c.c.) was reduced with lithium aluminiumhydride (5·7 g.) in ether (150 c.c.) to give propane-1,2-dithiol (6·18 g., 75%), b. p. 72—74°/25 mm., n_D^{20} 1·5335 (Found: thiol-S, 57·7. Calc. for $C_3H_8S_2$: thiol-S, 59·2%).

Propane-1,3-*dithiol*.—2-Thio-1,3-dithian [25] (15 g.) in tetrahydrofuran (100 c.c.) was reduced with lithium aluminium hydride (7 g.) in ether (70 c.c.) to give propane-1,3-dithiol (4·06 g., 37%), b. p. 76°/24 mm., n_D^{22} 1·5414 (Found: thiol-S, 57·2. Calc. for $C_3H_8S_2$: thiol-S, 59·2%).

Cyclohexane-trans-1,2-*dithiol*.—2-Thio-*trans*-cyclohexanodithiolan (III) [24] (8 g.) in tetrahydrofuran (75 c.c.) was reduced with lithium aluminium hydride (2·6 g.) in ether (50 c.c.), to give cyclohexane-*trans*-1,2-dithiol (5·6 g., 90%), b. p. 104—106°/18—19 mm., n_D^{20} 1·5515 (Found: thiol-S, 43·05. Calc. for $C_6H_{12}S_2$: thiol-S, 43·2%).

A mixture of the dithiol (0·86 g.), acetone (8 c.c.), and sulphuric acid (50 mg.) was left at room temperature for 12 hr. (a test portion then ceased to give a reaction for free thiol). The solvent was removed under reduced pressure, and the residue was taken up in chloroform, washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to a solid. Recrystallisation from aqueous methanol gave 2,2-*dimethyl*-trans-*cyclohexanodithiolan* (V) (0·79 g., 73%), as long needles, m. p. 37—38° (Found: C, 57·5; H, 8·6; S, 33·8. $C_9H_{16}S_2$ requires C, 57·4; H, 8·6; S, 34·0%).

DL-threo-3-*Bromobutan*-2-*ol*.—Potassium borohydride (7·2 g.) in water (100 c.c.) was added gradually (45 min.) to a stirred solution of 3-bromobutan-2-one (kindly provided by Mr. R. Grice) (50 g.), in methanol (150 c.c.), at 15—18°. The mixture was then neutralised with cold 2N-sulphuric acid, stirred for a further 15 min., and filtered to remove potassium sulphate. The latter was washed with ether, and the filtrate was saturated with salt and extracted with ether. The combined ether solutions were dried ($MgSO_4$) and distilled to give DL-*threo*-3-bromobutan-2-ol (25 g., 50%), b. p. 60—62°/20 mm., n_D^{19} 1·4733 (lit.,[26] b. p. 50°/13 mm., n_D^{20} 1·4771).

cis-2,3-*Epoxybutane*.—DL-*threo*-3-Bromobutan-2-ol (35 g.) was added during 1·5 hr. to a vigorously stirred solution of potassium hydroxide (55 g.) in water (27 c.c.) heated at 110—120°. The distillate, b. p. 58—60°, which was collected in an ice-cooled receiver, was dried ($MgSO_4$) and redistilled to give *cis*-2,3-epoxybutane (15·3 g., 96%), b. p. 59°, n_D^{18} 1·3812 (lit.,[11] b. p. 59·7°, n_D^{20} 1·3828).

trans-4,5-*Dimethyl*-2-*thiodithiolan* (VII).—*cis*-2,3-Epoxybutane (6 g.) was slowly added (15 min.) with shaking to a solution of potassium hydroxide (11·7 g.) and carbon disulphide (19 g.) in methanol (50 c.c.); the mixture was then set aside for 5 days. The solid which had gradually formed was collected and washed with water. Recrystallisation from light petroleum (b. p. 40—60°) gave the trans-*trithiocarbonate* (3·72 g., 27·2%), as yellow prisms, m. p. 40—41° (Found: C, 36·4; H, 5·3; S, 58·7. $C_5H_8S_3$ requires C, 36·6; H, 4·9; S, 58·5%); for $\nu_{max.}$ see Table.

threo-*Butane*-2,3-*dithiol*.—The trithiocarbonate (VII) (4·8 g.) in ether (50 c.c.) was reduced with lithium aluminium hydride (2·1 g.) in ether (30 c.c.) to give threo-*butane*-2,3-*dithiol* (1·65 g., 42%), b. p. 50—51°/22 mm., n_D^{21} 1·5315 (Found: C, 39·1, 40·1; H, 7·3, 8·2; S, 52·5; thiol-S, 51·8. $C_4H_{10}S_2$ requires C, 39·3; H, 8·2; S, 52·5%). It formed a *bisphenylurethane* which crystallised from aqueous methanol in long needles, m. p. 208—209° (Found: C, 60·0; H, 5·6; S, 17·8. $C_{18}H_{20}N_2O_2S_2$ requires C, 60·0; H, 5·6; S, 17·8%).

5,6-*Dideoxy*-1,3:2,4-*di*-O-*ethylidene*-5,6-*dimercapto*-L-*iditol* (XI).—5,6-Dideoxy-1,3:2,4-di-*O*-ethylidene-5,6-(thiocarbonyldithio)-L-iditol [5] (5 g.) in tetrahydrofuran (50 c.c.) was reduced with lithium aluminium hydride (1·3 g.) in ether (50 c.c.) to give a solid, which on recrystallisation from light petroleum (b. p. 60—80°) gave the *dithiol* (XI) (3·8 g., 88%) as granules, m. p. 80—81°, $[\alpha]_D^{22}$ −3·0° (*c*, 5) (Found: C, 44·9; H, 7·1; S, 24·4; thiol-S, 23·9. $C_{10}H_{18}O_4S_2$ requires C, 45·1; H, 6·8; S, 24·1%).

5,6-*Dideoxy*-1,2:3,4-*di*-O-*isopropylidene*-5,6-*dimercapto*-L-*gulitol* (XIII).—5,6-Dideoxy-1,2:3,4-di-*O*-isopropylidene-5,6-(thiocarbonyldithio)-L-gulitol [5] (3·5 g.) in ether (40 c.c.) was reduced with lithium aluminium hydride (0·9 g.) in ether (40 c.c.) to give the *dithiol* (XIII) (1·1 g., 33%), b. p. 92—94°/0·0005 mm., n_D^{20} 1·4963, $[\alpha]_D^{22}$ +37° (*c*, 10) (Found: C, 48·9; H, 7·7; S, 21·3; thiol-S, 18·7. $C_{12}H_{22}O_4S_2$ requires C, 49·0; H, 7·5; S, 21·8%).

5,6-*Dideoxy*-1,2:3,4-*di*-O-*isopropylidene*-5,6-*isopropylidenedithio*-L-*gulitol* (XIV).—A solution of the above dithiol (0·15 g.) in acetone (3 c.c.) containing sulphuric acid (0·02 g.) was set aside for 24 hr. and then evaporated under reduced pressure. The residue was taken up in

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[25] Mills and Saunders, *J.*, 1931, 537.

[26] House, *J. Amer. Chem. Soc.*, 1955, **77**, 5083.

chloroform, washed with sodium hydrogen carbonate solution and with water, then dried ($MgSO_4$), and evaporated to a solid, which on recrystallisation from aqueous methanol gave the *tri-isopropylidene* compound (XIV) as fine needles, m. p. 40—41° (Found: C, 54·4; H, 7·9; S, 19·3. $C_{15}H_{26}O_4S_2$ requires C, 53·8; H, 7·9; S, 19·2%).

1,2:5,6-*Dianhydro*-3,4-O-*isopropylidene*-D-*mannitol*.—The following procedure gives a much improved overall yield. A solution of toluene-*p*-sulphonyl chloride (64 g.) in pyridine (100 c.c.) was added dropwise during 5 hr. to a stirred solution of 3,4-*O*-isopropylidene-D-mannitol [27] (36 g.) in pyridine (100 c.c.), the temperature being allowed to rise to, but not exceed, 25°. The mixture was set aside for 12 hr., then poured into ice–water, and extracted with chloroform. The extract was washed twice with N-sulphuric acid at 0°, and then with water. It was dried (Na_2SO_4), filtered, cooled to −5°, and mixed with sodium methoxide solution [from sodium (8 g.) and methanol (120 c.c.)], also at −5°. The temperature was allowed to rise to 15° during 1 hr., and the gelatinous mass was then stirred into water and neutralised with carbon dioxide. The chloroform layer was isolated, washed with water, dried (Na_2SO_4), and distilled to give the dianhydro-compound (17·0 g., 56%), b. p. 80—82°/1 mm., n_D^{20} 1·4545 (lit.,[16] b. p. 75°/0·02 mm., n_D^{18} 1·4552).

1,2,5,6-*Tetradeoxy*-3,4-O-*isopropylidene*-1,2:5,6-*di*(*thiocarbonyldithio*)-L-*iditol* (XV).—1,2:5,6-Dianhydro-3,4-*O*-isopropylidene-D-mannitol (13 g.) was added with cooling and shaking to a solution of potassium hydroxide (22·8 g.) and carbon disulphide (36 g.) in methanol (100 c.c.); the mixture was then set aside. The solid which gradually appeared was collected after 24 hr. and washed with water. Recrystallisation from benzene–light petroleum (b. p. 40—60°) gave the *bistrithiocarbonate* (XV) (6·3 g., 25%), as yellow needles, m. p. 144—146° (Found: C, 36·0; H, 4·0; S, 52·2. $C_{11}H_{14}O_2S_6$ requires C, 35·7; H, 3·8; S, 52·0%). More of this slowly separated from the reaction mixture.

1,2,5,6-*Tetradeoxy*-3,4-O-*isopropylidene*-1,2,5,6-*tetramercapto*-L-*iditol* (XVI).—The above bistrithiocarbonate (6·12 g.) in tetrahydrofuran (80 c.c.) was reduced with lithium aluminium hydride (2·2 g.) in ether (50 c.c.) to give the *tetrathiol* (XVI) (3·1 g., 66%), b. p. 140—143°/0·0006 mm., n_D^{23} 1·5715, $[\alpha]_D^{22}$ +82° (*c*, 5·5) (Found: C, 37·7; H, 6·2; S, 43·8; thiol-S, 42·0. $C_9H_{18}O_2S_4$ requires C, 37·8; H, 6·3; S, 44·7%).

Reaction of a portion with acetic anhydride and pyridine for 24 hr. at room temperature, followed by dilution with water, gave a solid. Recrystallisation from aqueous methanol gave 1,2,5,6-*tetra-acetylthio*-1,2,5,6-*tetradeoxy*-3,4-O-*isopropylidene*-L-*iditol*, m. p. 105—107°, $[\alpha]_D^{22}$ +47·4° (*c*, 5) (Found: C, 44·4; H, 5·8; S, 28·6. $C_{17}H_{26}O_6S_4$ requires C, 44·9; H, 5·8; S, 28·2%); $\lambda_{max.}$ 230 mμ (ε 15,600) in EtOH.

3,4-*Di*-O-*acetyl*-1,2,5,6-*tetra-acetylthio*-1,2,5,6-*tetradeoxy*-L-*iditol* (XVII).—A mixture of 1,2,5,6-tetradeoxy-3,4-*O*-isopropylidene-1,2,5,6-tetramercapto-L-iditol (1·42 g.), ethanol (15 c.c.), and 0·4N-sulphuric acid (15 c.c.) was heated on a steam-bath, in a slow stream of nitrogen, until no more acetone was liberated (exit gases passed through aqueous 2,4-dinitrophenylhydrazine sulphate). The solution was concentrated under reduced pressure to remove ethanol, and then extracted with chloroform to give an oil (1·1 g.). This was dissolved in pyridine (4 c.c.) and acetic anhydride (4·2 g.) was added with cooling and shaking. After 2 days, water (2 c.c.) was added, and the mixture was concentrated to an oil, which was taken up in chloroform, washed with water, dried ($MgSO_4$), and evaporated to give a solid. Recrystallisation from aqueous methanol gave the *hexa-acetyl* compound (XVII), m. p. 126—128°, $[\alpha]_D^{22}$ −15° (*c*, 3) (Found: C, 43·5; H, 4·8; S, 26·0. $C_{18}H_{26}O_8S_4$ requires C, 43·4; H, 5·2; S, 25·7%); $\lambda_{max.}$ 230 mμ (ε 14,000) in EtOH.

3,4-*Dideoxy*-1,2:5,6-*di*-O-*isopropylidene*-3,4-(*thiocarbonyldithio*)-D-*mannitol* (XX) [or -D-*iditol* (XXI)].—A solution of 3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-D-talitol [17] (8 g.), potassium hydroxide (8 g.), and carbon disulphide (10 c.c.) in methanol (70 c.c.) was set aside for 23 days. The solution was then diluted with water (250 c.c.), warmed and stirred to expel the remaining carbon disulphide, and then cooled. The solid was collected and recrystallised from aqueous methanol, giving the *trithiocarbonate* (2 g., 27%) as yellow plates, m. p. 108—110° (Found: C, 46·6; H, 6·0; S, 28·5. $C_{13}H_{20}O_4S_3$ requires C, 46·4; H, 6·0; S, 28·6%). The yield could probably be improved by prolongation of the reaction time.

3,4-*Dideoxy*-1,2:5,6-*di*-O-*isopropylidene*-3,4-*dimercapto*-D-*mannitol* (XXII) [or -D-*iditol* (XXIII)].—The above trithiocarbonate (1·27 g.) in tetrahydrofuran (20 c.c.) was reduced with lithium aluminium hydride (0·39 g.) in ether (20 c.c.), and the product recrystallised from light

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[27] Wiggins, *J.*, 1946, 13.

petroleum (b. p. 60—80°), giving the *dithiol* (0·88 g., 51%) as needles, m. p. 133—135°, $[\alpha]_D^{22}$ −10° (*c*, 3·6) (Found: C, 49·1; H, 7·4; S, 21·5; thiol-S, 21·9. $C_{12}H_{22}O_4S_2$ requires C, 49·0; H, 7·5; S, 21·8%).

Reaction of Cyclopentene Oxide with Potassium Methyl Xanthate.—Cyclopentene oxide (8·4 g.) was added with shaking and cooling to a solution of potassium hydroxide (14 g.) and carbon disulphide (22·8 g.) in methanol (60 c.c.). No solid had appeared after storage for 4 weeks. The solution was then poured into water, excess of carbon disulphide was removed by a stream of nitrogen, and the solution was then acidified with 2N-hydrochloric acid. The oil which separated was taken up in chloroform, washed with water, and dried ($MgSO_4$). Removal of the solvent gave an oil (5·73 g.), which on distillation afforded a product containing *trans*-2-mercaptocyclopentanol, b. p. 98—100°/20 mm., n_D^{19} 1·5210 (Found: S, 25·9; thiol-S, 14·8. Calc. for $C_5H_{10}OS$: S, 27·1%). It was characterised as 2,4-dinitrophenyl *trans*-2-hydroxycyclopentyl sulphide, needles (from aqueous methanol), m. p. 114—115° (lit.,[18] m. p. 114—116°).

2-*Thio*-trans-*cyclopentanodithiolan* (XXX).—Cyclopentene sulphide [28] (0·55 g.) was added to a solution of potassium hydroxide (1·26 g.) and carbon disulphide (1·5 c.c.) in methanol (10 c.c.). After 4 days, the solid was recrystallised from methanol, giving the trans-*trithiocarbonate* (0·56 g., 58%) as yellow needles, m. p. 147° (Found: C, 40·8; H, 4·6; S, 54·5%; *M* in camphor, 173·8. $C_6H_8S_3$ requires C, 40·9; H, 4·6; S, 54·6%; *M*, 176·1); for $\nu_{max.}$ see Table.

Stability of Trimethylene Oxide towards Potassium Methyl Xanthate.—Trimethylene oxide [29] (1·1 g.) was added to a solution of potassium hydroxide (2 g.) and carbon disulphide (2·5 c.c.) in methanol (10 c.c.) and set aside for 8 weeks. Tests were made at intervals by dilution of a portion with water and extraction with chloroform, but the extracts were colourless, showing the absence of any trithiocarbonate (yellow).

Stability of Trimethylene Sulphide towards Potassium Methyl Xanthate.—A solution of trimethylene sulphide [30] (5 g.), potassium hydroxide (9·2 g.), and carbon disulphide (15·2 g.) in methanol (40 c.c.) was set aside for 7 weeks and occasionally tested, as described above, for the formation of a trithiocarbonate, but the chloroform extracts were colourless. Heating in a sealed tube at 100° for 6 hr. gave a similar result.

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[28] Goodman, Benitez, and Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 1680.
[29] Shirley, " Preparation of Organic Intermediates," Wiley, New York, 1951, p. 292.
[30] Bennett and Hock, *J.*, 1927, 2496.