228. *Dithiols. Part XXII.*[1] *Isopropylidene Derivatives and Cyclic Thiocarbonates from* trans-*Dithiols and from* trans-*Mercapto-alcohols.*

By M. Kyaw and L. N. Owen.

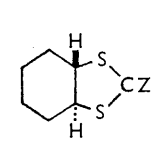
The above types of derivatives (2,2-dimethyl-1,3-dithiolans, 1,3-dithiolan-2-ones, and 1,3-dithiolan-2-thiones) are readily formed by reaction of acetone, carbonyl chloride, and potassium methyl xanthate, respectively, with vicinal *trans*-dithiols attached to a six-membered ring; they are not formed from cyclopentane-*trans*-1,2-dithiol. In contrast, vicinal *trans*-mercapto-alcohols give 2,2-dimethyl-1,3-oxathiolans and 1,3-oxathiolan-2-ones even when attached to a five-membered ring. New heterocyclic analogues of the highly strained *trans*-bicyclo[3,3,0]octane system have thus been obtained [(XXVIII)—(XXXII)].

In a five- or a six-membered ring system the *cis*-form of a vicinal diol can usually be converted readily into a cyclic acetal or ketal (a 1,3-dioxolan), whilst the *trans*-isomer is unaffected by the normal procedure. Cyclohexane-*trans*-1,2-diol can be made to react with acetone [2] and with benzaldehyde,[3] though only under forcing conditions, and two stereoisomeric tri-*O*-isopropylideneinositols have been described,[4] each of which contains one *trans*-fused dioxolan ring; in the latter compounds the presence of the first two *O*-isopropylidene groups (both *cis*) probably deforms the cyclohexane ring in such a way as to facilitate the final condensation of acetone with the remaining *trans*-diol system, but even so this last stage is difficult and does not proceed to completion. In contrast, the *trans*-fused 1,3-dithiolan systems in the compounds (I) [1] and (IV) [5] are formed very easily under mild conditions from the corresponding dithiols, and recently the first example of a *trans*-fused 1,3-oxathiolan ring, in the compound (VI), has been reported.[6] The cyclic trithiocarbonates (II) [1] and (V) [5] can also be made without difficulty from the appropriate epoxide and potassium methyl xanthate, and an even more striking instance of the ease with which highly strained sulphur-containing rings are formed is afforded by the trithiocarbonate (VII).[7] In order to study more fully the factors involved in the formation of such heterocycles, some new types of dithiols were required, and the opportunity was also taken to synthesise a number of vicinal *trans*-mercapto-alcohols so that their behaviour in cyclisation reactions could be compared with that of the dithiols.

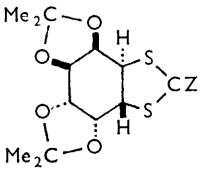
Reaction of 4,5-epoxycyclohexene with potassium methyl xanthate gave the trithiocarbonate (IX) which was reduced with lithium aluminium hydride to cyclohex-4-ene-*trans*-1,2-dithiol. Tetralin-*trans*-2,3-dithiol was similarly prepared from the trithiocarbonate (XII), and cyclopentane-*trans*-1,2-dithiol from the trithiocarbonate (VII), which, as shown earlier,[1] can be made only from cyclopentene sulphide and *not* from cyclopentene oxide. Three further examples have now been found of epoxides which fail to yield trithiocarbonates containing two *trans*-fused five-membered rings, namely 3,4-epoxytetrahydrothiophen dioxide (XIV), 3,4-epoxytetrahydrofuran (XVI), and 1,2-epoxyindane (XX). We therefore attempted to obtain the corresponding episulphides from them. Methods such as reaction with thiourea or a thiocyanate, which convert epoxides into episulphides in six-membered ring systems, fail or give very poor yields with cyclopentene oxide,[8] and were likewise unsuccessful with these three epoxides. Cyclopentene sulphide can, however, be obtained easily by alkaline hydrolysis of *trans*-2-acetylthiocyclopentyl

[1] Part XXI, S. M. Iqbal and L. N. Owen, *J.*, 1960, 1030.
[2] W. R. Christian, C. J. Gogek, and C. B. Purves, *Canad. J. Chem.*, 1951, **29**, 911.
[3] A. Rieche, E. Schmitz, W. Schade, and E. Beyer, *Chem. Ber.*, 1961, **94**, 2926.
[4] S. J. Angyal and C. G. Macdonald, *J.*, 1952, 686.
[5] G. E. McCasland, S. Furuta, A. Furst, L. F. Johnson, and J. N. Shoolery, *J. Org. Chem.*, 1963, **28**, 456.
[6] G. E. McCasland, S. Furuta, and A. Furst, *J. Org. Chem.*, 1964, **29**, 724.
[7] C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J.*, 1946, 1050.
[8] L. Goodman and B. R. Baker, *J. Amer. Chem. Soc.*, 1959, **81**, 4924.

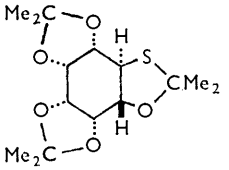
acetate,[9] prepared [10] by reaction of cyclopentene oxide with thiolacetic acid and subsequent acetylation. Of the three epoxides, only 1,2-epoxyindane (XX) reacted readily with thiolacetic acid, and acetylation of the product gave *trans*-1-acetylthioindan-2-yl acetate (XXI); acid hydrolysis of this furnished *trans*-1-mercaptoindan-2-ol, the orientation of which was proved by desulphurisation to give indan-2-ol. Increasing the nucleophilic power of the reagent by the addition of some potassium thiolacetate enabled an attack to be made on the two less reactive epoxides; under these conditions *O*-acetylation of the resulting hydroxy-thiolacetate occurred spontaneously, completely in the case of 3,4-epoxytetrahydrothiophen dioxide (XIV) which gave the diacetate (XV), and partially in the case of 3,4-epoxytetrahydrofuran (XVI), the product from which was therefore further acetylated to give the diacetate (XVII). In earlier studies on the alkaline deacetylation of



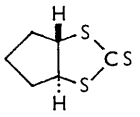
(I : Z = Me_2)
(II : Z = S)
(III : Z = O)



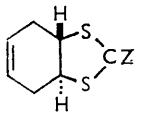
(IV : Z = Me_2)
(V : Z = S)



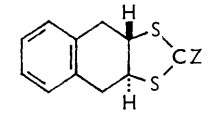
(VI)



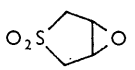
(VII)



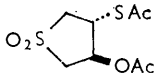
(VIII : Z = Me_2)
(IX : Z = S)
(X : Z = O)



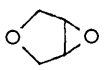
(XI : Z = Me_2)
(XII : Z = S)
(XIII : Z = O)



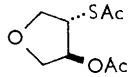
(XIV)



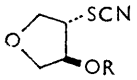
(XV)



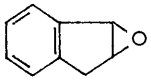
(XVI)



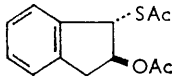
(XVII)



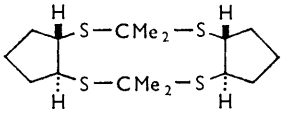
(XVIII : R = H)
(XIX : R = SO_2Me)



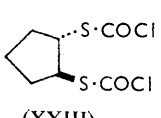
(XX)



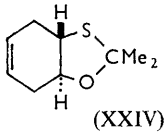
(XXI)



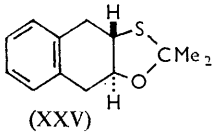
(XXII)



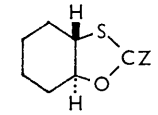
(XXIII)



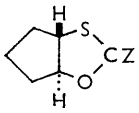
(XXIV)



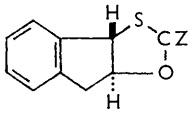
(XXV)



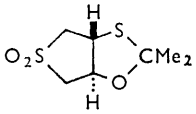
(XXVI : Z = Me_2)
(XXVII : Z = O)



(XXVIII : Z = Me_2)
(XXIX : Z = O)



(XXX : Z = Me_2)
(XXXI : Z = O)



(XXXII)

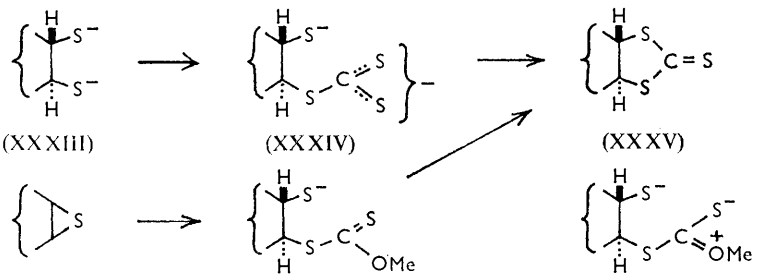
acetylated mercaptoalcohols,[10,11] the extent to which cyclic sulphides are formed was assessed by quantitative estimation of the liberation of thiol and of acetyl groups during the course of the reaction. When this method was applied to the three diacetyl derivatives (XV), (XVII), and (XXI) the thiol value in each case attained the theoretical figure for complete liberation and remained so when both acetyl groups had been entirely hydrolysed, thus indicating that no episulphide was being formed; furthermore, alkaline hydrolysis

[9] L. Goodman, A. Benitez, and B. R. Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 1680.
[10] J. S. Harding and L. N. Owen, *J.*, 1954, 1528.
[11] J. S. Harding and L. N. Owen, *J.*, 1954, 1536.

on a preparative scale gave only the corresponding mercapto-alcohol. The latter compounds, which were required for the condensation reactions described later, were also obtained by acid hydrolysis of the diacetates; additionally, two of them were prepared by fission of the epoxides (XIV) and (XX) with potassium hydrogen sulphide. It is interesting that an attempt to prepare a furanose episulphide by alkaline hydrolysis of methyl 2,5-di-*O*-acetyl-3-acetylthio-3-deoxy-β-D-xylofuranoside, an analogue of the diacetate (XVII), also failed,[12] although the method was successful with a pyranoside.[13]

Goodman and Baker [8] have shown that cyclopentene sulphide is formed by the alkaline hydrolysis of *trans*-2-thiocyanatocyclopentyl methanesulphonate. Since the methanesulphonyloxy-group would be expected to undergo intramolecular displacement much more readily than the acetoxy-group, it was thought that this method might be more successful. 3,4-Epoxytetrahydrofuran (XVI) was therefore converted into the *trans*-thiocyanato-alcohol (XVIII) by reaction with thiocyanic acid, and thence into the methanesulphonate (XIX), but no episulphide could be obtained from the latter.

Cyclohex-4-ene-*trans*-1,2-dithiol and tetralin-*trans*-2,3-dithiol both reacted with acetone, containing a trace of sulphuric acid, to give the dithiolans (VIII) and (XI), and with carbonyl chloride and pyridine they gave the cyclic dithiocarbonates (X) and (XIII). The molecular weights of all four products were in agreement with these monomeric structures. Cyclohexane-*trans*-1,2-dithiol similarly gave the cyclic dithiocarbonate (III). In contrast, cyclopentane-*trans*-1,2-dithiol gave with acetone a comparatively high-melting solid which was one of the diastereoisomers of the dimeric compound (XXII) (*meso*-form shown); furthermore, with carbonyl chloride this dithiol gave a product which appeared to be mainly the bischloroformate (XXIII). This difference in behaviour between the six- and the five-membered ring dithiols was also apparent in their reactions with potassium methyl xanthate; at room temperature, cyclohexane-*trans*-1,2-dithiol, cyclohex-4-ene-*trans*-1,2-dithiol, and tetralin-*trans*-2,3-dithiol readily gave the trithiocarbonates (II), (IX), and (XII), but cyclopentane-*trans*-1,2-dithiol gave none of the derivative (VII) even at 100°. The failure of this last reaction is of particular interest because the trithiocarbonate (VII) *can* be obtained by treatment of cyclopentene sulphide with xanthate.[1] To explain these observations it is necessary to consider the likely course of the reaction of potassium methyl xanthate with a dithiol (XXXIII). The first step



presumably involves attack by one of the ionised thiol groups on the xanthate, with expulsion of methoxide and formation of the mesomeric ion (XXXIV), followed by intramolecular displacement of sulphide ion to give the trithiocarbonate (XXXV). The structure of the corresponding intermediate in the reaction sequence from the episulphide (XXXVI) must be essentially (XXXVII) with only a small contribution from the other canonical form (XXXVIII). The intermediates (XXXIV) and (XXXVII) are in fact related in the same way as a carboxylate anion is to an ester, and nucleophilic attack on the thiocarbonyl carbon atom in the cyclisation stage will occur more readily with

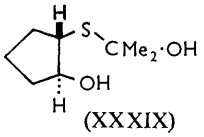
[12] C. D. Anderson, L. Goodman, and B. R. Baker, *J. Amer. Chem. Soc.*, 1959, **81**, 898.
[13] J. E. Christensen and L. Goodman, *J. Amer. Chem. Soc.*, 1961, **83**, 3827.

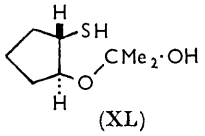
(XXXVII) than with (XXXIV). This difference in ease of attack is evidently not critical when the six-membered ring compounds are involved, but becomes so when the highly strained *trans*-junction has to be formed between two five-membered rings. With regard to the sequence postulated for the reaction of the dithiol (XXXIII), the alternative, in which sulphide ion would be expelled from the reagent in the first stage, is not only inherently less likely but is ruled out because the intermediate would then be (XXXVII) irrespective of whether a dithiol or an episulphide was used.

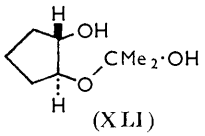
For a study of the reactions of mercapto-alcohols, two more compounds, *trans*-6-mercaptocyclohex-3-en-1-ol and *trans*-3-mercaptotetralin-2-ol were prepared by fission of the corresponding epoxides with potassium hydrogen sulphide. These two mercapto-alcohols, and also *trans*-2-mercaptocyclohexanol, condensed with acetone under mild conditions to give the monomeric isopropylidene derivatives (XXIV), (XXV), and (XXVI). A vicinal *trans*-mercapto-alcohol system attached to a six-membered ring therefore behaves like the corresponding dithiol, and unlike the *trans*-diol; this is also exemplified by Meloy's observation [14] that *trans*-2-mercaptocyclohexanol condenses with carbonyl chloride to form the cyclic monothiolcarbonate (XXVII).

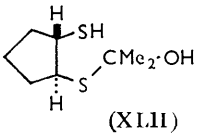
In view of the formation of the dimeric product (XXII) from cyclopentane-*trans*-1,2-dithiol and acetone, it was very surprising to find that *trans*-2-mercaptocyclopentanol gave the monomeric product (XXVIII). *trans*-1-Mercaptoindan-2-ol and *trans*-tetrahydro-4-mercaptothiophen-3-ol 1,1-dioxide likewise gave the monomeric isopropylidene derivatives (XXX) and (XXXII). Also in contrast to the behaviour of the corresponding dithiol, *trans*-2-mercaptocyclopentanol with carbonyl chloride gave the monothiolcarbonate (XXIX); *trans*-1-mercaptoindan-2-ol gave a similar derivative (XXXI).

It is remarkable that these heterocyclic analogues of the strained *trans*-bicyclo[3,3,0]-octane system should be formed so easily from a *trans*-mercapto-alcohol when they are not produced from a *trans*-diol or a *trans*-dithiol attached to a five-membered ring. Considering, for example, the isopropylidene derivative (XXVIII) there are two ways by which it could be derived from *trans*-2-mercaptocyclopentanol, but since ketones react with simple thiols much more readily than they do with alcohols [15] it might appear that the reaction would proceed through the intermediate (XXXIX) rather than (XL); evidence has in fact been cited [16] which has been taken to indicate that it is the thiol group in 2-mercaptoethanol which reacts first with steroidal ketones. In reversible reactions of this type, however, even the isolation of a postulated intermediate does not necessarily prove that it lies on


(XXXIX)


(XL)


(XLI)


(XLII)

the preferred path to the final product, and with a mercapto-alcohol it is clearly unsound to consider the relative reactivities of the thiol and the alcohol function with regard only to the first stage. On the contrary, when a strained fused ring system is being produced it is the final stage which is likely to be decisive. On this basis the intermediate (XL) is more probable. This should cyclise more readily than the corresponding intermediate (XLI) from cyclopentane-*trans*-1,2-diol, on the reasonable assumption that the distance between the reacting centres, which is slightly more in (XL) than in (XLI), is of less significance than the nucleophilic power of the thiol group; furthermore, the alternative intermediate (XXXIX) not only lacks the nucleophilic advantage but also has an even greater distance between the centres which would have to react. In the intermediate (XLII), from cyclopentane-*trans*-1,2-dithiol, this distance is greater still, and must account for the lack of

[14] C. R. Meloy, *Trans. Illinois State Acad. Sci.*, 1963, **56**, 146.
[15] J. Hine, "Physical Organic Chemistry," McGraw-Hill, London, 2nd edn., 1962, p. 253.
[16] C. Djerassi and M. Gorman, *J. Amer. Chem. Soc.*, 1953, **75**, 3704; cf. G. Rosenkranz, S. Kaufmann, and J. Romo, *ibid.*, 1949, **71**, 3689.

cyclisation in spite of the possession of the thiol group; although the distance is the same as that involved in the final stage of the formation of the cyclic trithiocarbonate (VII) from cyclopentene sulphide [cf. (XXXVII)] the reacting species are different, and in the latter case the attack is by the much more strongly nucleophilic thiol anion. Thus with the five-membered ring compounds there appears to be a rather fine balance between electronic and steric effects which decides whether ring closure can occur.

Experimental

Analyses were by Miss J. Cuckney and the staff of the Organic Microanalytical Laboratory; molecular weights were determined in benzene, either ebullioscopically or by isothermal distillation at 37°.

trans-4,5-(*Thiocarbonyldithio*)*cyclohexene* (IX).—4,5-Epoxycyclohexene [17] (6·5 g.) was added, with cooling, to a solution of potassium hydroxide (13·5 g.) and carbon disulphide (26·5 g.) in methanol (85 c.c.). The mixture was left at room temperature for 24 hr. and the yellow solid was collected, washed with water, and recrystallised from methanol to give the *trithiocarbonate* (8·6 g.), m. p. 146° (Found: C, 44·6; H, 4·5; S, 51·0. $C_7H_8S_3$ requires C, 44·65; H, 4·3; S, 51·1%).

Cyclohex-4-*ene*-trans-1,2-*dithiol*.—The above trithiocarbonate (8·6 g.) in tetrahydrofuran (75 c.c.) was slowly added to a stirred solution of lithium aluminium hydride (2·6 g.) in ether (50 c.c.). Isolation of the product by the procedure previously described [1] gave the dithiol (5·7 g.), b. p. 70—72°/8mm., n_D^{19} 1·6845 (Found: C, 49·4; H, 6·7; S, 43·6; thiol-S, 43·7. $C_6H_{10}S_2$ requires C, 49·25; H, 6·9; S, 43·8%).

Tetralin-trans-2,3-*dithiol*.—Reduction of *trans*-2,3-(thiocarbonyldithio)tetralin [18] (5 g.) in tetrahydrofuran (140 c.c.) with lithium aluminium hydride (1·6 g.) in ether (40 c.c.) gave the dithiol (3·55 g.), m. p. 87° (from methanol) (Found: C, 60·9; H, 6·2; S, 32·5; thiol-S, 32·6. Calc. for $C_{10}H_{12}S_2$: C, 61·2; H, 6·2; S, 32·7%). Hauptmann and Bobbio [18] describe the compound as an oil, and record no thiol value.

Cyclopentane-trans-1,2-*dithiol*.—*trans*-1,2-(Thiocarbonyldithio)cyclopentane [1] (13 g.) in tetrahydrofuran (200 c.c.) was reduced with lithium aluminium hydride (5 g.) in ether (100 c.c.) to give the *dithiol* (7·2 g.), b. p. 102—103°/30 mm., n_D^{20} 1·5519 (Found: C, 45·1; H, 7·5; S, 47·6; thiol-S, 47·6. $C_5H_{10}S_2$ requires C, 44·8; H, 7·5; S, 47·8%).

Attempted Preparation of Trithiocarbonates from Certain Epoxides.—3,4-Epoxytetrahydrofuran [19] (0·6 g.) was added to potassium hydroxide (1·1 g.) and carbon disulphide (1·5 g.) in methanol (10 c.c.). The solution was left for several weeks at room temperature. Test portions were occasionally removed, diluted with water, and extracted with chloroform. The extracts were colourless, showing the absence of any trithiocarbonate.

Similar results were obtained with 3,4-epoxytetrahydrothiophen dioxide [20] and with 1,2-epoxyindane.[21]

trans-1-*Acetylthioindan*-2-*yl Acetate* (XXI).—Thiolacetic acid (3·2 g.) was slowly added, with cooling, to 1,2-epoxyindane [21] (5·0 g.); the mixture was set aside for 3 days and the excess of thiolacetic acid then removed under reduced pressure. Acetic anhydride (6·6 g.) and a trace of sulphuric acid were added to the residue, and 2 days later the solution was treated with crushed ice, stirred for 3 hr., and extracted with chloroform to give an oil. On distillation this gave trans-1-*acetylthioindan*-2-*yl acetate* (5·6 g.), b. p. 124—126°/10^{-2} mm., n_D^{19} 1·5535 (Found: C, 62,3; H, 5·9; S, 12·9. $C_{13}H_{14}O_3S$ requires C, 62·4; H, 5·6; S, 12·8%).

trans-4-*Acetylthiotetrahydro*-3-*thienyl Acetate* 1,1-*Dioxide* (XV).—When 3,4-epoxytetrahydrothiophen dioxide [20] (6·0 g.) was added to thiolacetic acid (7·5 g.) no heat was evolved. The mixture was heated at 80° for 5 hr.; when it was cooled, the solid which crystallised out was the epoxide. Potassium thiolacetate (0·5 g.) was then added to the same mixture, and after 4 hr. at 85° the solution was diluted with chloroform, washed with aqueous sodium hydrogen carbonate, dried, and evaporated. Crystallisation of the residue from ether gave the *diacetyl*

[17] M. E. Ali and L. N. Owen, *J.*, 1958, 1066.
[18] H. Hauptmann and F. O. Bobbio, *Chem. Ber.*, 1960, **93**, 2187.
[19] W. Reppe, *Annalen*, 1955, **596**, 138.
[20] B. Loev, *J. Org. Chem.*, 1961, **26**, 4394.
[21] W. F. Whitmore and A. I. Gebhart, *J. Amer. Chem. Soc.*, 1942, **64**, 912.

compound (5·7 g.), m. p. 98°, $\lambda_{max.}$ 229 mμ (ε 3500) in EtOH (Found: C, 38·2; H, 4·7; S, 25·1. $C_8H_{12}O_5S_2$ requires C, 38·1; H, 4·8; S, 25·45%).

trans-4-*Acetylthiotetrahydrofuran*-3-*yl Acetate* (XVII).—A mixture of 3,4-epoxytetrahydrofuran [19] (6·5 g.), thiolacetic acid (6·1 g.), and potassium thiolacetate (0·5 g.) was heated at 90° for 5 hr. and then worked up as in the preceding experiment. Distillation gave an oil (8·5 g.), b. p. 86—88°/10^{-3} mm., n_D^{24} 1·5196, which was essentially trans-4-*acetylthiotetrahydrofuran*-3-*ol* (Found: C, 44·0; H, 5·8; S, 19·4. $C_6H_{10}O_3S$ requires C, 44·4; H, 6·2; S, 19·8%), though the infrared spectrum showed the presence of *O*-acetyl ($\nu_{max.}$ 1739) as well as hydroxyl ($\nu_{max.}$ 3556) and *S*-acetyl ($\nu_{max.}$ 1688 cm.$^{-1}$).

Acetylation of this product (5·8 g.) with acetic anhydride (9·4 g.) and toluene-*p*-sulphonic acid (0·2 g.) for 24 hr. at room temperature gave trans-4-*acetylthiotetrahydrofuran*-3-*yl acetate* (6·0 g.), b. p. 81—83°/10^{-3} mm., n_D^{23} 1·4975, $\nu_{max.}$ 1740 and 1684 cm.$^{-1}$, $\lambda_{max.}$ 231 mμ (ε 3750) in EtOH (Found: C, 46·7; H, 5·7; S, 16·9. $C_8H_{12}O_4S_2$ requires C, 47·0; H, 5·9; S, 16·7%).

Quantitative Alkaline Hydrolysis of Diacetyl Derivatives of Mercapto-alcohols.—Determinations were carried out in 50% aqueous dioxan at 0° by the procedure described previously.[10] The Table shows, at the time specified, the extent to which the two acetyl groups have been removed and the one thiol group liberated.

(XXI)	*t* (min.)	2	8	15	23	38	84	120	180
	Acetyl	0·4	0·8	1·2	1·45	1·7	1·9	1·95	2·0
	Thiol	0·3	0·6	0·85	0·95	1·0	1·0	1·0	1·0
(XV)	*t* (min.)	2	5	8	14	26	43	63	
	Acetyl	0·5	0·9	1·05	1·3	1·65	1·9	2·05	
	Thiol	0·3	0·6	0·7	0·8	0·95	1·0	1·0	
(XVII)	*t* (min.)	2	4	6	12	20	32	67	180
	Acetyl	0·4	0·7	0·9	1·15	1·4	1·65	1·95	2·0
	Thiol	0·3	0·5	0·6	0·8	0·9	0·95	1·0	1·0

trans-*Tetrahydro*-4-*thiocyanatofuran*-3-*ol* (XVIII).—To a mixture of potassium thiocyanate (11·5 g.), crushed ice (50 g.), and ether (35 c.c.), 85% phosphoric acid (15·7 g.) was added in portions, with shaking. The red ethereal layer was then separated and added to a solution of 3,4-epoxytetrahydrofuran (3·4 g.) in ether (10 c.c.) at 0°. The mixture was dried ($MgSO_4$) and stored at 0° for 2 days. Distillation then gave the *thiocyanate* (3·6 g.), b. p. 124—125°/3 mm., n_D^{21} 1·5300, $\nu_{max.}$ 3357 (OH), 2149 (SCN), and 2073 cm.$^{-1}$ (very weak, NCS) in $CHCl_3$ (Found: C, 41·2; H, 5·3; N, 9·4. $C_5H_7NO_2S$ requires C, 41·4; H, 4·9; N, 9·6%).

trans-*Tetrahydro*-4-*thiocyanatofuran*-3-*yl Methanesulphonate* (XIX).—A solution of the preceding compound (1·5 g.) and methanesulphonyl chloride (1·5 g.) in pyridine (7 c.c.) was kept for 2 days at 0° and then poured into cold 2N-hydrochloric acid (35 c.c.). Extraction with dichloromethane gave the *methanesulphonate* (1·75 g.), b. p. 146—148°/10^{-3} mm., n_D^{21} 1·5160, $\nu_{max.}$ 2165 (SCN), 1370 and 1351 cm.$^{-1}$ (O·SO_2) (Found: C, 32·3; H, 4·4; S, 29·0. $C_6H_9NO_4S$ requires C, 32·3; H, 4·1; S, 28·7%).

When this compound was stirred with N-sodium hydroxide under nitrogen at room temperature for 24 hr., acidification and extraction with dichloromethane gave no recognisable product.

trans-1-*Mercaptoindan*-2-*ol*.—(i) A suspension of *trans*-1-acetylthio-2-acetoxyindane (4·4 g.) in N-sodium hydroxide (70 c.c.) was stirred vigorously under nitrogen for 8 hr. at room temperature. A small amount of solid (possibly disulphide) was removed by filtration, and the solution was acidified to pH 4 with hydrochloric acid and extracted with chloroform to give trans-1-*mercaptoindan*-2-*ol* (2·6 g., 90%), b. p. 97—99°/10^{-2} mm., n_D^{22} 1·6020 (Found: C, 65·3; H, 6·1; S, 19·35; thiol-S, 19·1. $C_9H_{10}OS$ requires C, 65·0; H, 6·1; S, 19·3%).

(ii) A solution of *trans*-1-acetylthioindan-2-yl acetate (1·85 g.) in 5% methanolic hydrogen chloride (30 c.c.) was left for 4 days at room temperature and then distilled to give the mercapto-alcohol (1·05 g., 85%), b. p. 98—100°/10^{-2} mm., n_D^{22} 1·6022 (Found: thiol-S, 19·0%).

(iii) To a solution of potassium hydroxide (3·3 g.) in ethanol (20 c.c.), saturated with hydrogen sulphide at 0°, a solution of 1,2-epoxyindane (7·6 g.) in ethanol (20 c.c.) was added. Whilst a slow stream of hydrogen sulphide was maintained, the mixture was kept at room temperature for 4 hr. and then poured on to crushed ice (150 g.), acidified with hydrochloric acid, and extracted with ether to give the mercapto-alcohol (8·9 g., 92%), b. p. 98—100°/10^{-2} mm., n_D^{22} 1·6020.

Desulphurisation. *trans*-1-Mercaptoindan-2-ol (0·5 g.), prepared by method (ii), was boiled under reflux for 2 hr. with a suspension of Raney nickel (*ca.* 5 g.) in ethanol (10 c.c.). Evaporation of the filtered solution gave indan-2-ol (0·3 g.), m. p. 69° (lit.,[21] 69°), *p*-nitrobenzoate, m. p. 139° (lit.,[21] 139°). The thiol prepared by method (iii) gave the same results.

trans-*Tetrahydro*-4-*mercaptofuran*-3-*ol.*—Deacetylation of *trans*-4-acetylthiotetrahydrofuran-3-yl acetate (1·0 g.) in 5% methanolic hydrogen chloride (25 c.c.) for 4 days at room temperature, followed by distillation, gave the *mercapto-alcohol* (0·55 g.), b. p. 62—64°/10^{-2} mm., n_D^{22} 1·5275 (Found: C, 39·7; H, 7·0; S, 26·4; thiol-S, 26·4. $C_4H_8O_2S$ requires C, 40·0; H, 6·7; S, 26·7%).

trans-*Tetrahydro*-4-*mercaptothiophen*-3-*ol* 1,1-*Dioxide.*—(i) Deacetylation of *trans*-4-acetylthiotetrahydro-3-thienyl acetate 1,1-dioxide (0·7 g.) as above gave the *mercapto-alcohol* (0·4 g.), m. p. 105° (from ethanol) (Found: C, 28·3; H, 4·6; S, 38·4; thiol-S, 38·0. $C_4H_8O_3S_2$ requires C, 28·6; H, 4·8; S, 38·1%).

(ii) 3,4-Epoxytetrahydrothiophen 1,1-dioxide (1·4 g.) was disolved in 0·15N-potassium hydroxide (85 c.c.), previously saturated with hydrogen sulphide, and kept at 50° for 4 hr. under hydrogen sulphide. Acidification and extraction with ether gave the same mercapto-alcohol (1·35 g.), m. p. 104—105° (Found: thiol-S, 38·0%).

trans-6-*Mercaptocyclohex*-3-*en*-1-*ol.*—4,5-Epoxycyclohexene [17] (3·6 g.) was treated, as described above for the similar reaction on 1,2-epoxyindane, with potassium hydrogen sulphide, prepared from potassium hydroxide (2·1 g.) in ethanol (35 c.c.). The *mercapto-alcohol* (3·4 g.) had b. p. 68—70°/45 mm., n_D^{18} 1·5437 (Found: C, 55·5; H, 7·9; S, 24·7; thiol-S, 24·7. $C_6H_{10}OS$ requires C, 55·4; H, 7·7; S, 24·6%).

trans-3-*Mercaptotetralin*-2-*ol.*—Similar treatment of 2,3-epoxytetralin [17] (1·5 g.) gave the *mercapto-alcohol* (1·3 g.), m. p. 90—91° (from methanol) (Found: C, 66·7; H, 6·7; S, 17·5; thiol-S, 17·5. $C_{10}H_{12}OS$ requires C, 66·6; H, 6·7; S, 17·8%).

On one occasion, when insufficient hydrogen sulphide was present, the main product was *bis*-(3-*hydroxy*-2-*tetralin*) *sulphide*, m. p. 171—172° (from ethanol) (Found: C, 73·5; H, 7·0; S, 10·1; thiol-S, nil. $C_{20}H_{22}O_2S$ requires C, 73·6; H, 6·8; S, 9·8%).

Reactions of Dithiols and of Mercapto-alcohols with Acetone.—General Method. A solution of the compound in 10—20 parts of AnalaR acetone, containing 0·1% of sulphuric acid, was set aside for 24 hr. Any solid derivative which had then crystallised was collected, and the solution was concentrated under reduced pressure and poured into aqueous sodium hydrogen carbonate solution. If solid, the product was collected and washed with water; otherwise it was extracted with chloroform and distilled.

Cyclohex-4-ene-*trans*-1,2-dithiol (0·6 g.) gave trans-4,5-(*isopropylidenedithio*)*cyclohexene* (VIII) (0·6 g.), b. p. 76—78°/10^{-2} mm., m. p. 22—23° (Found: C, 58·3; H, 7·3; S, 34·2%; *M*, 188·7. $C_9H_{14}S_2$ requires C, 58·0; H, 7·6; S, 34·4%; *M*, 186·3).

Tetralin-*trans*-2,3-dithiol (1·15 g.) gave trans-2,3-(*isopropylidenedithio*)*tetralin* (XI) (1·1 g.), m. p. 160—161° (from methanol) (Found: C, 66·2; H, 6·7; S, 27·4%; *M*, 234·5. $C_{13}H_{16}S_2$ requires C, 66·0; H, 6·8; S, 27·1%; *M*, 236·4).

Cyclopentane-*trans*-1,2-dithiol gave 2,2,7,7-*tetramethyl*-4,5:9,10-*biscyclopentano*-1,3,6,8-*tetrathiacyclodecane* (XXII) (0·95 g.), m. p. 197—198° (from methanol) (Found: C, 54·8; H, 8·45; S, 36·8%; *M*, 344·2. $C_{16}H_{28}S_2$ requires C, 55·1; H, 8·1; S, 36·8%; *M*, 348·6).

trans-2-Mercaptocyclohexanol [22] (0·9 g.) gave 2,2-*dimethyl*-trans-4,5-*cyclohexano*-1,3-*oxathiolan* (XXVI) (0·8 g.), b. p. 53—55°/10^{-2} mm., n_D^{15} 1·4945 (Found: C, 62·7; H, 9·0; S, 18·5%; *M*, 170·0. $C_9H_{16}OS$ requires C, 62·7; H, 9·4; S, 18·6%; *M*, 172·3).

cis-2-Mercaptocyclohexanol [23] (0·9 g.) gave 2,2-*dimethyl*-cis-4,5-*cyclohexano*-1,3-*oxathiolan* (0·7 g.); b. p. 54—55°/10^{-2} mm., n_D^{20} 1·5000 (Found: C, 62·7; H, 9·0; S, 18·3%; *M*, 170·9).

trans-6-Mercaptocyclohex-3-en-1-ol (1·0 g.) gave trans-4,5-(*isopropylideneoxythio*)*cyclohexene* (XXIV) (0·9 g.), b. p. 56—57°/0·1 mm., n_D^{20} 1·5142 (Found: C, 63·4; H, 8·4; S, 19·0%; *M*, 173·2. $C_9H_{14}OS$ requires C, 63·5; H, 8·3; S, 18·8%; *M*, 170·2).

trans-3-Mercaptotetralin-2-ol (0·6 g.) gave trans-2,3-(*isopropylideneoxythio*)*tetralin* (XXV) (0·5 g.), m. p. 115° (from ethanol) (Found: C, 70·5; H, 7·1; S, 14·8. $C_{13}H_{16}OS$ requires C, 70·8; H, 7·3; S, 14·5%).

trans-2-Mercaptocyclopentanol [9,10] (1·2 g.) gave trans-1,2-(*isopropylideneoxythio*)*cyclopentane* (XXVIII) (0·5 g.), b. p. 56—58°/10^{-2} mm., n_D^{22} 1·5136 (Found: C, 60·3; H, 9·1; S, 20·1%; *M*, 160·9. $C_8H_{14}OS$ requires C, 60·6; H, 8·9; S, 20·2%; *M*, 158·2).

[22] C. C. J. Culvenor, W. Davies, and N. S. Heath, *J.*, 1949, 278.
[23] H. Behringer and W. Kley, *Annalen*, 1955, **595**, 160.

trans-1-Mercaptoindan-2-ol (0·25 g.) gave trans-4,5-*dihydro*-2,2-*dimethylindeno*[3′,2′:4,5]-1,3-*oxathiole* (XXX) (0·15 g.), m. p. 41—42° (from methanol) (Found: C, 69·8; H, 7·0; S, 15·5%; *M*, 208·9. $C_{12}H_{14}OS$ requires C, 69·85; H, 6·8; S, 15·5%; *M*, 206·3).

trans-Tetrahydro-4-mercaptothiophen-3-ol 1,1-dioxide (0·5 g.) gave trans-*tetrahydro*-3,4-(*isopropylideneoxythio*)*thiophen* 1,1-*dioxide* (XXXII) (0·4 g.), m. p. 165° (from methanol) (Found: C, 40·3; H, 6·0; S, 31·0%; *M*, 213·3. $C_7H_{12}O_3S_2$ requires C, 40·4; H, 5·8; S, 30·8; *M*, 208·3).

Reactions with Carbonyl Chloride.—General method. A solution of the compound in 5—10 parts of toluene, containing pyridine (*ca.* 5 mol.) was treated at 0° with 12·5% carbonyl chloride in toluene (*ca.* 2 mol.), and kept at 0° for 2 hr. The solution was then washed with water, with 2N-hydrochloric acid, again with water, dried, and evaporated under reduced pressure. Solid products were recrystallised from methanol.

(With T. J. Adley). Cyclohexane-*trans*-1.2-dithiol [1] (1·0 g.) gave trans-4,5-cyclohexano-1,3-dithiolan-2-one (III) (0·8 g.), needles, m. p. 106—107°, $\lambda_{max.}$ 251 mμ (ε 2500 in EtOH), $\nu_{max.}$ 1790, 1748, 1715, 1652, and 1600 cm.$^{-1}$ (in CCl_4) (Found: C, 48·1; H, 5·9%; *M*, 180·0. $C_7H_{10}OS_2$ requires C, 48·2; H, 5·8%; *M*, 174·3).

Cyclohex-4-ene-*trans*-1,2-dithiol (0·6 g.) gave trans-4,5-(*carbonyldithio*)*cyclohexene* (X) (0·6 g.), m. p. 108—109° (Found: C, 48·5; H, 4·6; S, 37·0%; *M*, 167·4. $C_7H_8OS_2$ requires C, 48·8; H, 4·7; S, 37·2%; *M*, 172·2).

Tetralin-*trans*-2,3-dithiol (0·3 g.) gave trans-2,3-(*carbonyldithio*)*tetralin* (XIII) (0·35 g.), m. p. 165° (Found: C, 59·3; H, 4·45; S, 28·5%; *M*, 220·0. $C_{11}H_{10}OS_2$ requires C, 59·4; H, 4·5; S, 28·8%; *M*, 222·3).

Cyclopentane-*trans*-1,2-dithiol (0·4 g.) gave an unstable oil, mainly 1,2-bischlorocarbonylthiocyclopentane (XXIII) (0·35 g.), b. p. 84—86°/10^{-2} mm., n_D^{18} 1·5723 (Found: C, 32·9; H, 4·6; Cl, 23·1. Calc. for $C_7H_8O_2S_2Cl_2$: C, 31·5; H, 3·0; Cl, 26·3%).

trans-2-Mercaptocyclohexanol (1·2 g.) gave *trans*-4,5-cyclohexano-1,3-oxathiolan-2-one (XXVII) (1·2 g.), b. p. 83—85°/10^{-2} mm., n_D^{15} 1·5232 (Found: C, 52·9; H, 6·0; S, 20·1%; *M*, 156·1. Calc. for $C_7H_{10}O_2S$: C, 53·15; H, 6·4; S, 20·3%; *M*, 158·1). Lit.[14] m. p. 27°.

trans-2-Mercaptocyclopentanol (0·9 g.) gave trans-4,5-*cyclopentano*-1,3-*oxathiolan*-2-*one* (XXIX) (0·3 g.), b. p. 93—95°/10^{-3} mm., n_D^{19} 1·5235 (Found: C, 49·8; H, 5·3; S, 22·5%; *M*, 140·4. $C_6H_8O_2S$ requires C, 50·0; H, 5·6; S, 22·2%; *M*, 144·2).

trans-1-Mercaptoindan-2-ol (0·4 g.) gave trans-4,5-*dihydroindeno*[3′,2′:4,5]-1,3-*oxathiol*-2-*one* (XXXI) (0·4 g.), plates, m. p. 88—89° (Found: C, 64·5; H, 4·5; S, 16·5; *M*, 196·2. $C_{10}H_8O_2S$ requires C, 64·5; H, 4·2; S, 16·7%; *M*, 192·2).

Reactions with Potassium Methyl Xanthate.—General method. The dithiol was added to a solution of potassium hydroxide (0·45 g.) and carbon disulphide (0·55 g.) in methanol (5 c.c.). After 4 days at room temperature, the trithiocarbonate was filtered off, washed with water, and crystallised from methanol.

Cyclohexane-*trans*-1,2-dithiol (0·3 g.) gave *trans*-4,5-cyclohexano-1,3-dithiolan-2-thione (II) (0·25 g.), m. p. 169° (lit.,[7] 169°).

Cyclohex-4-ene-*trans*-1,2-dithiol (0·15 g.) gave *trans*-4,5-(thiocarbonyldithio)cyclohexene (IX) (0·1 g.), m. p. and mixed m. p. 146°.

Tetralin-*trans*-2,3-dithiol (0·3 g.) gave *trans*-2,3-(thiocarbonyldithio)tetralin (XII) (0·3 g.), m. p. and mixed m. p. 192—193°.

Cyclopentane-*trans*-1,2-dithiol (0·25 g.) gave no trithiocarbonate even after 2 weeks; chloroform extracts of test portions, diluted with water, were colourless. Boiling the reaction mixture under reflux for 3 hr. also gave a negative result.

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