

Dithiols. Part XXVI.¹ Conversion of Aliphatic and Alicyclic Epoxides into Trithiocarbonates

By Md. Erfan Ali, Nabil G. Kardouche, and Leonard N. Owen,* Department of Chemistry, Imperial College, London SW7 2AY

The reactions of *meso*-2,3-epoxybutane, 1,2-epoxycyclohexane, and 2,3-epoxy-*trans*-decalin with sodium *O*-ethyl xanthate, to give the corresponding trithiocarbonates, have been studied under a variety of conditions. Products from the decalin epoxide included 3 α -ethoxythiocarbonylthio-*trans*-decalin-2 β -ol, 3 α -ethoxythiocarbonylthio-*trans*-decalin-2 β -thiol, 3 α -mercapto-*trans*-decalin-2 β -ol, and the *meso*- and the DL-form of 3 α ,3 α' -thiobis-(*trans*-decalin-2 β -ol). Trithiocarbonates were obtained from all three epoxides by reaction with sodium *NN*-diethyldithiocarbamate: under mild conditions the intermediate *NN*-diethylthiocarbamoylthio-compounds were isolated. Cyclisation of *trans*-2-*N*-phenylthiocarbamoylthiocyclohexanol by treatment with thionyl chloride or toluene-*p*-sulphonyl chloride resulted in partial desulphurisation, and gave *trans*-2-phenyliminoperhydro-1,3-benzoxathiolan: some other approaches to a stereospecific synthesis of a *cis*-dithiol system are outlined.

REDUCTION of a cyclic trithiocarbonate is a useful method for the synthesis of a dithiol,² but the mechanism by which an epoxide (1) reacts with the salt of an *O*-alkyl

¹ Part XXV, L. N. Owen and M. B. Rahman, *J.C.S. Perkin I*, 1974, 2413.

² S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1960, 1030.

³ A. M. Creighton and L. N. Owen, *J. Chem. Soc.*, 1960, 1024.

xanthate to give a trithiocarbonate (6) involves several intermediates³ of which only the episulphide (4) has ever been isolated, and that merely on two occasions.^{4,5}

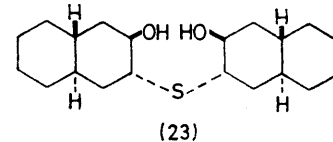
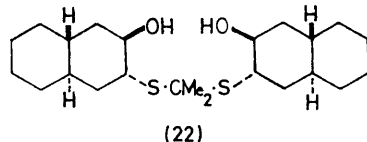
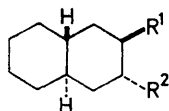
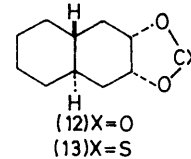
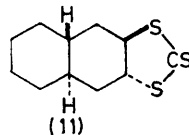
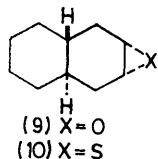
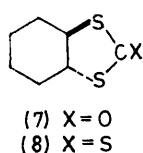
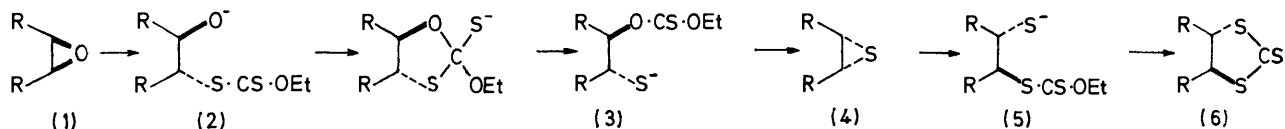
⁴ M. Kojima, M. Watanabe, and T. Taguchi, *Tetrahedron Letters*, 1968, 839.

⁵ M. V. Jesudason and L. N. Owen, *J.C.S. Perkin I*, 1974, 2024.

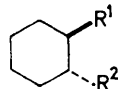
Although the postulated mechanism is in accord with stereochemical evidence,⁵⁻⁷ further substantiation by isolation of any other intermediate has hitherto been lacking.

meso-2,3-Epoxybutane (1; R = Me) is known^{2,6} to give the DL-trithiocarbonate (6; R = Me) on reaction with an excess of potassium methyl xanthate. By

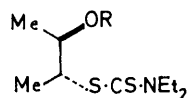
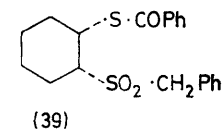
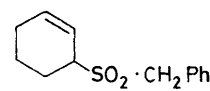
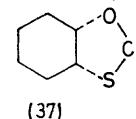
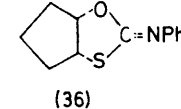
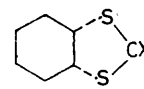
compound is intriguing, and a likely explanation is that the ethoxythiocarbonyloxy-group displaced in the stage (3) \rightarrow (4) reacts (in the more stable ethoxycarbonylthio-form) with the intermediate episulphide in a manner analogous to the reaction of the episulphide with xanthate; this would then produce the cyclic dithiolcarbonate.



- (14) R¹ = OH, R² = S · CS · OEt
(15) R¹ = SH, R² = S · CS · OEt
(16) R¹ = OH, R² = SH
(17) R¹ = OAc, R² = SAc
(18) R¹ = OH, R² = SCN
(19) R¹ = OH, R² = NCS
(20) R¹ = O · SO₂Me R² = SCN
(21) R¹ = OH, R² = S · CS · NEt₂



- (26) R¹ = OH, R² = S · CS · NEt₂
(27) R¹ = OTs, R² = S · CS · NEt₂
(28) R¹ = OH, R² = S · CS · NHPH
(29) R¹ = OAc, R² = S · CS · NHPH
(30) R¹ = OAc, R² = S · C(SAc) · NPh
(31) R¹ = OH, R² = S · CH₂ Ph
(32) R¹ = OH, R² = SO₂CH₂ Ph
(33) R¹ = OTs, R² = SO₂CH₂ Ph



- (24) R = H
(25) R = Ts

reaction of this epoxide with 1 mol. equiv. of sodium ethyl xanthate under mild conditions, and separation of the mixture of products by t.l.c., a small quantity of the intermediate DL-*threo*-3-(ethoxythiocarbonylthio)-butan-2-ol (2; R = Me) has now been isolated.* When 1,2-epoxycyclohexane was treated with 1 mol. equiv. of the xanthate reagent, no corresponding intermediate was detected; the trithiocarbonate (8) was isolated in 44% yield (*i.e.* nearly theoretical, based on the amount of xanthate) together with a trace of *trans*-1,2-carbonyl-dithiocyclohexane (7). The formation of the latter

* In the steroid field, hydroxy-xanthates of type (2) have been synthesised by other methods⁷ and, if of suitable configuration, have been converted into episulphides by treatment with base.

† *trans*-Decalin is conventionally written with H-8a in the β -configuration. Each derivative mentioned in the present work, being racemic, contained of course an equal amount of the 8aH-enantiomer.

2,3-Epoxy-*trans*-decalin (9) on reaction with xanthate would be expected to give, by diaxial opening of the intermediate episulphide, the 2 β ,3 α -trithiocarbonate (11),[†] but this occurred considerably less readily than the corresponding reaction with 1,2-epoxycyclohexane. Under the mild conditions (ambient temperature) under which the latter epoxide gives a good yield of trithiocarbonate⁸ the decalin epoxide (9) gave, almost quantitatively, 3 α -(ethoxythiocarbonylthio)-*trans*-decalin-2 β -ol (14); from an experiment at a higher temperature, the trithiocarbonate (11) (23%), the alcohol (14) (26%), and 3 α -(ethoxythiocarbonylthio)-*trans*-decalin-2 β -thiol (15)

⁶ C. G. Overberger and A. Drucker, *J. Org. Chem.*, 1964, **29**, 360.

⁷ D. A. Lightner and C. Djerassi, *Tetrahedron*, 1965, **21**, 583.

⁸ C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, 1946, 1050.

(10%) were obtained. The isolation of the thiol (15) is interesting because compounds of this type, although assumed to be intermediates in the mechanistic sequence [cf. (5)], have never been prepared even by other methods. From another experiment, carried out for a longer time, a diminished yield (17%) of trithiocarbonate and 3 α -mercapto-*trans*-decalin-2 β -ol (16) (6%) was obtained; mercapto-alcohols (or their oxidation products), no doubt formed by solvolysis of intermediates such as (14), have been reported as by-products in similar reactions in the carbohydrate field.^{4,5,9}

The mercapto-alcohol (16) was synthesised by treatment of the decalin epoxide (9) with ethanolic potassium hydrogen sulphide, but unlike certain analogous compounds of alicyclic¹⁰ and steroidal¹¹ types, which readily form cyclic isopropylidene derivatives, it reacted with acetone to give one diastereoisomer (DL- or *meso*-) of the acetal (22) (*meso*-form shown), the constitution being based on elemental analysis, molecular weight (by isothermal distillation), and n.m.r. and i.r. spectra (hydroxy-group); remarkably, the highest mass peak in the mass spectrum was at *m/e* 226, which corresponds to the simple isopropylidene derivative of the mercapto-alcohol (16), yet the other evidence clearly rules this out.

In a further experiment on the reaction of the decalin epoxide (9) with xanthate, a mixture of stereoisomeric sulphides was isolated, and separated by t.l.c. into the *meso*-form (23) and the DL-form, though individual configurations were not determined. This type of product has been encountered in carbohydrate studies^{4,9} and is evidently formed by interaction of the mercapto-alcohol (16) with the epoxide. The mass spectra of the two diastereoisomers showed the same fragmentation pattern, though the peak intensities were different.

Treatment of the epoxide (9) with thiocyanic acid gave the thiocyanato-alcohol (18), together with a small quantity of the isothiocyanato-alcohol (19), readily separated by t.l.c. The constitution of the main product was confirmed by reduction with lithium aluminium hydride to give an excellent yield of the mercapto-alcohol (16). It also formed a methanesulphonate (20), and on reaction of this derivative with base (a method used¹² for the preparation of cyclopentene sulphide and of a carbohydrate episulphide) a product was obtained which, from the elemental analysis and mass spectrum, was identified as the episulphide (10); however its amorphous character and failure to give any of the trithiocarbonate (11) on treatment with xanthate cast some doubt on its formulation as the monomer, even though the highest *m/e* value corresponded to the expected structure. Reaction of the decalin epoxide

⁹ M. V. Jesudason and L. N. Owen, *J.C.S. Perkin I*, 1974, 2019.

¹⁰ M. Kyaw and L. N. Owen, *J. Chem. Soc.*, 1965, 1298.

¹¹ K. Takeda, T. Komeno, J. Kawanami, S. Ishihara, H. Kadokawa, H. Tokura, and H. Itani, *Tetrahedron*, 1965, **21**, 329.

¹² L. Goodman and B. R. Baker, *J. Amer. Chem. Soc.*, 1959, **81**, 4924; J. E. Christensen and L. Goodman, *ibid.*, 1961, **83**, 3827.

¹³ L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 1952, 817; J. S. Harding and L. N. Owen, *ibid.*, 1954, 1528; M. Kyaw and L. N. Owen, *ibid.*, 1964, 6252; L. Goodman, A. Benitez, and B. R. Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 1680.

(9) with potassium thiocyanate gave a similar result. Furthermore, reaction of 3 α -(ethoxythiocarbonylthio)-*trans*-decalin-2 β -ol (14), 3 α -thiocyanato-*trans*-decalin-2 β -ol (18), or 3 α -acetylthio-*trans*-decalin-2 β -yl acetate (17) with base (methods which have been used to obtain steroid^{7,11} and other¹³ episulphides) gave no recognisable products.

Trithiocarbonates have been prepared by reaction of an epoxide with carbon disulphide in the presence of a tertiary amine, under pressure,¹⁴ and it therefore seemed probable that an *NN*-dialkyldithiocarbamate salt would act as an analogous but more convenient reagent. Reaction of an excess of sodium *NN*-diethyldithiocarbamate with *meso*-2,3-epoxybutane and with 1,2-epoxycyclohexane in aqueous ethanol at ambient temperature afforded the trithiocarbonates (6; R = Me) (19%) and (8) (29%). When only 1 mol. equiv. of reagent was used, DL-*threo*-3-(*NN*-diethylthiocarbamoylthio)butan-2-ol (24) (37%) and *trans*-2-(*NN*-diethylthiocarbamoylthio)cyclohexanol (26) (98%), respectively, were obtained, and a similar product (21) was isolated almost quantitatively under these conditions from the decalin epoxide (9). Conversion of the alcohol (26) into the toluene-*p*-sulphonate (27), followed by solvolysis in ethanolic potassium acetate, was expected¹⁵ to give the cyclic dithiolcarbonate (34), but in fact the alcohol (26) was regenerated; 2-(*NN*-diethylthiocarbamoylthio)-1-methylpropyl toluene-*p*-sulphonate (25) behaved similarly.

The failure to obtain the *cis*-fused dithiolcarbonate (34) was particularly disappointing because no general methods are available for the stereospecific synthesis of alicyclic *cis*-dithiols, though stereoselective syntheses of cyclohexane- and cyclopentane-*cis*-1,2-dithiol have been described.¹⁶ A method¹⁷ for the synthesis of *cis*-2-mercaptocyclopentanol involves conversion of cyclopentane-*trans*-1,2-diol into the mono(phenylthiourethane), which on reaction with thionyl chloride furnishes the phenylimino-compound (36); the *cis*-mercapto-alcohol is then obtained by hydrolysis. We therefore treated *trans*-2-mercaptocyclohexanol with 1 mol. equiv. of phenyl isothiocyanate and obtained the phenyldithiourethane (28), the constitution of which was confirmed by the i.r. spectrum (hydroxy-group) and by acetylation, which gave a mixture, separable by fractional crystallisation, of the *O*-acetate (29) and the diacetyl derivative (30). Reaction of the dithiourethane (28) with thionyl chloride was expected to give the cyclised product (35), but led only to the monothio-compound (37) (retention of configuration is assumed) and elemental sulphur; the same products were formed when an attempt was made to prepare the *O*-toluene-*p*-sulphonate of the dithiourethane.

¹⁴ J. A. Durden, H. A. Stansbury, and W. H. Catlette, *J. Amer. Chem. Soc.*, 1960, **82**, 3082.

¹⁵ Cf. S. Ishiguro and S. Tejima, *Chem. and Pharm. Bull. (Japan)*, 1968, **16**, 1567.

¹⁶ J. D. Willett, J. R. Grunwell, and G. A. Berchtold, *J. Org. Chem.*, 1968, **33**, 2297.

¹⁷ L. Goodman, A. Benitez, C. D. Anderson, and B. R. Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 6582.

The synthesis of a *cis*-dithiol derivative by intermolecular S_N2 displacement on a *trans*-2-(alkylthio)cyclohexyl toluene-*p*-sulphonate is unlikely to proceed because of neighbouring group participation by the alkylthio-function, which would lead, through an intermediate episulphonium ion, to a *trans*-dithiol derivative. If, however, the neighbouring group contained the sulphur atom in a state in which it could not participate, such as in the form of a sulphone, this approach would evidently be more helpful. Accordingly, *trans*-2-benzylthiocyclohexanol (31) was converted, with hydrogen peroxide, into the sulphone (32) and thence into *trans*-2-benzylsulphonylcyclohexyl toluene-*p*-sulphonate (33). When this derivative was treated with potassium thiobenzoate in boiling dimethylformamide, elimination occurred to give benzyl cyclohex-2-enyl sulphone (38), but in boiling ethanol the product was a readily separable mixture of this and the substitution product, *cis*-2-(benzoylthio)cyclohexyl benzyl sulphone (39). It has been reported¹⁸ that some sulphones can be reduced to sulphides by the use of a large excess of lithium aluminium hydride, but the i.r. spectrum of the product so obtained from the sulphone (39), although devoid of absorption attributable to the thiobenzoate function, still showed strong bands indicative of the persistence of the sulphone group.

Oxidation of *trans*-2-benzylthiocyclohexanol with sodium periodate gave both possible stereoisomeric sulphoxides.

EXPERIMENTAL

I.r. spectra were measured for solutions in chloroform, and ¹H n.m.r. spectra for solutions in deuteriochloroform (Varian A60 or HA100 instrument). Mass spectra were recorded with a Perkin-Elmer 270 or A.E.I. MS9 instrument at 70 eV. The adsorbent for t.l.c. was Kieselgel GF₂₅₄ (Merck); that for column chromatography was silica gel MFC (Hopkin and Williams). Organic extracts were dried over magnesium sulphate, and solvents were removed under reduced pressure below 50°. Petroleum refers to the fraction of b.p. 40–60°.

2,3-Epoxy-*trans*-decalin.—A solution of 3-chloroperbenzoic acid (10.35 g) in chloroform (150 ml) was slowly added to a solution of *trans*- Δ^2 -octalin (5.45 g purified¹⁹ through the dibromide) in chloroform (20 ml) at 0°. The cooling bath was then removed, and the mixture was set aside for 1 h before being filtered. The filtrate was washed twice with aqueous 10% sodium hydroxide and with water, and was then dried and concentrated. Distillation of the residue gave the epoxide (5.0 g), b.p. 108° at 22 mmHg, n_D^{20} 1.4582 (lit.,¹⁹ b.p. 105° at 21 mmHg, n_D^{25} 1.4835).

3 α -Mercapto-*trans*-decalin-2 β -ol (16).—A solution of 2,3-epoxy-*trans*-decalin (5.0 g) in ethanol (25 ml) was slowly added to a solution of potassium hydroxide (4.0 g) in ethanol (25 ml), previously saturated with hydrogen sulphide at 0°. The stream of hydrogen sulphide was maintained while the mixture was allowed to attain ambient temperature, and the flask was then stoppered and left overnight. The solution was then mixed with

crushed ice (200 g) and acidified by gradual addition of 2N-sulphuric acid; it was then extracted with ether, and the extracts were washed with water, dried, and concentrated to give the *mercapto-alcohol* (5.7 g), needles (from petroleum), m.p. 76°, ν_{\max} 3550, 3380, and 2580 cm⁻¹ (Found: C, 64.6; H, 9.8; S, 17.2; thiol S, 17.2. C₁₀H₁₈OS requires C, 65.0; H, 9.7; S, 17.2%).

Acetylation (acetic anhydride-pyridine) afforded the *diacetyl* derivative (17) as an oil, ν_{\max} 1738 and 1690 cm⁻¹ (Found: C, 62.3; H, 8.3; S, 12.1. C₁₄H₂₂O₃S requires C, 62.2; H, 8.2; S, 11.85%).

Treatment of the mercapto-alcohol, in acetic acid, with a slight excess of 0.1N-iodine, followed by dilution with water, precipitated 3 α ,3 α' -*dithiobis*-(*trans*-*decalin*-2 β -ol), m.p. 114–115° (from ether-petroleum) (Found: C, 65.0; H, 9.2; S, 17.4%; M^+ , 370. C₂₀H₃₄O₂S₂ requires C, 64.8; H, 9.25; S, 17.3%; M , 370).

A solution of the mercapto-alcohol (0.3 g) in acetone (15 ml) containing sulphuric acid (0.1 ml) was set aside for 24 h, then concentrated, mixed with aqueous sodium hydrogen carbonate, and extracted with ether to give 3 α ,3 α' -*isopropylidenedithiobis*-(*trans*-*decalin*-2 β -ol) (22), m.p. 229–230° (from acetone), ν_{\max} 3680 cm⁻¹, τ 6.0 (2H, m, CH-O), 6.95 (2H, m, CH-S), 8.45 (2H, s, OH; removed by D₂O), 8.75 (6H, s, Me), and 8.0–9.0 (*ca.* 28H, m), *m/e* 226 (41%), 152 (100), 136 (17), 135 (38), 134 (35), 121 (23), 109 (11), 108 (13), 107 (11), 96 (13), 95 (40), 94 (26), 93 (38), 92 (21), 91 (29), 81 (29), 79 (29), 77 (13), 75 (21), 74 (13), 70 (17), 67 (50), 55 (29), 43 (34), and 41 (42) (Found: C, 66.5; H, 9.8; S, 15.45%; M , by isothermal distillation, 430. C₂₈H₄₀O₂S₂ requires C, 66.8; H, 9.7; S, 15.55%; M , 412.5).

Reactions of Epoxides with Xanthate.—The reagent was prepared by addition of carbon disulphide (30% excess) to ethanolic sodium ethoxide.

(i) To the reagent, from sodium (0.3 g) and ethanol (10 ml), a solution of *meso*-2,3-epoxybutane² (1.0 g) in ethanol (5 ml) was added at 0°. The mixture was kept at 0° for 1 h, and was then diluted with water and extracted with chloroform. The extracts were washed with water, then dried and evaporated to leave an oil, which by t.l.c. (chloroform) gave a small amount of yellow crystals, m.p. 40–41°, identified as DL-2,3-thiocarbonyldithiobutane by comparison (i.r. spectrum and mixed m.p.) with an authentic specimen (lit.,² m.p. 40–41°), and DL-threo-3-(*ethoxythiocarbonylthio*)butan-2-ol, an oil (0.1 g), ν_{\max} 3540 and 3370 cm⁻¹ (Found: C, 43.1; H, 7.0; S, 32.9%; M^+ , 194. C₇H₁₄O₂S₂ requires C, 43.3; H, 7.25; S, 33.0%; M , 194).

(ii) A mixture of 1,2-epoxycyclohexane (0.36 g) and the reagent, from sodium (84 mg) and ethanol (10 ml), was kept at -5° for 24 h, then filtered to remove a crop of *trans*-1,2-thiocarbonyldithiocyclohexane (8). The filtrate was diluted with water and extracted with chloroform to give an oil, which by t.l.c. (chloroform-petroleum, 1:2) gave a second crop of trithiocarbonate (total 0.30 g), m.p. 169–170° (lit.,⁸ 169°) and a trace of *trans*-1,2-carbonyldithiocyclohexane (7), m.p. 104–106° (lit.,²⁰ 109–110°), identified by the i.r. spectrum.

(iii) 2,3-Epoxy-*trans*-decalin (1.5 g) in ethanol (25 ml) was added, at 0°, to the reagent, from sodium (2.3 g) and ethanol (50 ml). The mixture was kept at 0° for 1 h, then

¹⁸ F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, 1951, **73**, 2251; W. P. Weber, P. Stromquist, and T. I. Ito, *Tetrahedron Letters*, 1974, 2595.

¹⁹ W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, 1961, **83**, 606.

²⁰ T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc. (C)*, 1967, 807.

at ambient temperature for 120 h, and was worked up, as described for the reaction with epoxybutane, to give (t.l.c. in chloroform) *3 α -ethoxythiocarbonylthio-trans-decalin-2 β -ol* (14), an oil (2.6 g), ν_{\max} 3550 and 3480 cm^{-1} (Found: C, 56.85; H, 8.0; S, 23.3%; M^+ , 274. $\text{C}_{13}\text{H}_{22}\text{O}_2\text{S}_2$ requires C, 56.9; H, 8.1; S, 23.4%; M , 274).

(iv) The preceding experiment was repeated, but the mixture was kept at ambient temperature for 24 h and then boiled under reflux for 2 h. The product was separated by t.l.c. (chloroform-petroleum, 1:2) into *2 β ,3 α -thiocarbonyldithio-trans-decalin* (11) (1.1 g), m.p. 126–127° (from ether-petroleum) (Found: C, 53.9; H, 6.6; S, 39.2. $\text{C}_{11}\text{H}_{16}\text{S}_3$ requires C, 54.0; H, 6.6; S, 39.35%), *3 α -ethoxythiocarbonylthio-trans-decalin-2 β -thiol* (15) (0.3 g) as an oil, ν_{\max} 2580 cm^{-1} (Found: C, 53.7; H, 7.6; S, 32.8%; M^+ , 290. $\text{C}_{13}\text{H}_{22}\text{OS}_3$ requires C, 53.7; H, 7.6; S, 33.1%; M , 290), and *3 α -ethoxythiocarbonylthio-trans-decalin-2 β -ol* (1.4 g), identical (i.r. spectrum) with that described above.

(v) The preceding experiment was repeated, but the mixture was boiled under reflux for 24 h. The products were the trithiocarbonate (11) (0.39 g), m.p. 126–127°, and *3 α -mercapto-trans-decalin-2 β -ol* (16) (0.11 g), m.p. 72–75° (i.r. spectrum identical with that of material prepared from 2,3-epoxy-trans-decalin).

(vi) 2,3-Epoxy-trans-decalin (1.5 g) in ethanol (15 ml) was added at 0° to a solution of potassium ethyl xanthate (1.6 g) in ethanol (50 ml). The mixture was kept at 0° for 1 h, then at ambient temperature for 48 h, and was finally boiled under reflux for 20 h. The product, by t.l.c. (chloroform), furnished the two stereoisomers (*meso*- and *DL*-) of *3 α ,3 α' -thiobis-(trans-decalin-2 β -ol)*; one (0.2 g) had m.p. 204–209° (from ether-petroleum), ν_{\max} 3550 and 3320 cm^{-1} (Found: C, 70.8; H, 10.0; S, 9.6%; M^+ , 338. $\text{C}_{20}\text{H}_{34}\text{O}_2\text{S}$ requires C, 70.95; H, 10.1; S, 9.5%; M , 338), and the other (0.65 g) had m.p. 157° (from ether-petroleum), ν_{\max} 3350 and 3340 cm^{-1} (Found: C, 70.8; H, 10.0; S, 9.7%; M^+ , 338).

3 α -Thiocyanato-trans-decalin-2 β -ol (18).—88% Phosphoric acid (30 g) was added in portions to a solution of potassium thiocyanate (20 g) in water (30 ml), covered with a layer of ether (100 ml), at 0°, with shaking. The ether was then removed, washed with water, dried, and added to a solution of 2,3-epoxy-trans-decalin (1.5 g) in ether (10 ml). The mixture was set aside for 24 h and was then washed with aqueous sodium carbonate and with water. Evaporation of the dried organic solution gave a solid residue, which was separated by t.l.c. (chloroform) into the *thiocyanate* (1.5 g), m.p. 69–70° (from petroleum), ν_{\max} 3550, 3400, and 2175 cm^{-1} (Found: C, 62.4; H, 7.95; N, 6.6; S, 15.25%; M^+ , 211. $\text{C}_{11}\text{H}_{17}\text{NOS}$ requires C, 62.5; H, 8.1; N, 6.6; S, 15.2%; M , 211), and *3 α -isothiocyanato-trans-decalin-2 β -ol* (19) (0.1 g), an oil, ν_{\max} 3550, 3360, and 2110 cm^{-1} (Found: C, 62.45; H, 8.0; N, 6.4; S, 15.1%; M^+ , 211).

Reaction of the thiocyanate (0.21 g) with methanesulphonyl chloride (0.57 g) in pyridine (10 ml) for 24 h at 0° gave *3 α -thiocyanato-trans-decalin-2 β -yl methanesulphonate* (20) (0.28 g), an oil (t.l.c. in chloroform), ν_{\max} 2175, 1345, and 1165 cm^{-1} (Found: C, 50.0; H, 6.9; N, 4.7; S, 22.3. $\text{C}_{12}\text{H}_{19}\text{NO}_3\text{S}_2$ requires C, 49.8; H, 6.6; N, 4.8; S, 22.2%).

Reduction of the thiocyanate (0.21 g) with lithium aluminium hydride (76 mg) in ether (20 ml) at ambient temperature for 1 h gave *3 α -mercapto-trans-decalin-2 β -ol*, m.p. 74–75°, identical with that described above (Found: C, 64.4; H, 9.5; S, 17.0%).

2 α ,3 α -Epithio-trans-decalin (10).—(i) A mixture of *3 α -thiocyanato-trans-decalin-2 β -yl methanesulphonate* (0.24 g), aqueous 5% potassium hydroxide (40 ml), and ethanol (40 ml) was stirred for 24 h; a colourless solid which had then been formed was collected and subjected to t.l.c. (chloroform) to give a main fraction (0.12 g) of the *epi-sulphide* as a glass, ν_{\max} 1440, 1350, 1140, 980, and 945 cm^{-1} m/e 168 (M^+ , 13%), 137 (13), 136 (100), 135 (18), 134 (22), 121 (37), 108 (20), 107 (33), 95 (74), 94 (50), 93 (44), 92 (17), 91 (26), 82 (13), 81 (28), 80 (22), 79 (45), 77 (20), 69 (17), 68 (13), 67 (80), 57 (17), 55 (22), 54 (14), 53 (13), 43 (13), and 41 (48) (Found: C, 71.0; H, 9.3; S, 18.8. $\text{C}_{10}\text{H}_{16}\text{S}$ requires C, 71.3; H, 9.6; S, 19.1%).

(ii) A solution of 2,3-epoxy-trans-decalin (0.8 g) and potassium thiocyanate (3.4 g) in ethanol (50 ml) was boiled under reflux for 15 h. It was then cooled, diluted with water, and extracted with chloroform to give an oil, the i.r. spectrum of which was similar to that of the *epi-sulphide* obtained in the preceding experiment, but t.l.c. failed to effect purification.

Reactions of Epoxides with Sodium NN-Diethylthiocarbamate Trihydrate.—(i) A solution of *meso*-2,3-epoxybutane (0.5 g) and the carbamate (7.8 g) in water (45 ml) was stirred at 0° for 2 h and then at ambient temperature for 48 h. It was then extracted with chloroform, and the extract was washed with water, dried, and concentrated. The residue was purified by t.l.c. (ether) to give *DL*-2,3-thiocarbonyldithiobutane (0.2 g), m.p. and mixed m.p. 40–41°, identified also by the i.r. spectrum.

(ii) A solution of *meso*-2,3-epoxybutane (1.0 g) and the carbamate (3.1 g) in ethanol (25 ml) and water (15 ml) was kept at 0° for 1 h followed by 1 h at ambient temperature. Dilution with water and extraction with chloroform gave an oil, which by t.l.c. (chloroform) furnished *DL*-threo-3-(*NN*-diethylthiocarbamoylthio)butan-2-ol (24) (1.2 g), ν_{\max} 3550 and 3375 cm^{-1} (Found: C, 49.1; H, 8.6; N, 6.3; S, 28.8%; M^+ , 221. $\text{C}_8\text{H}_{19}\text{NOS}_2$ requires C, 48.8; H, 8.65; N, 6.3; S, 29.0%; M , 221).

(iii) A mixture of 1,2-epoxycyclohexane (0.5 g), the carbamate (2.6 g), and water (50 ml) was stirred at ambient temperature for 72 h, and then extracted with chloroform to give a semi-solid. This was triturated with ether and filtered, to obtain *trans*-1,2-thiocarbonyldithiocyclohexane (0.2 g), m.p. 169–171°; the filtrate was concentrated, and the residue was purified by t.l.c. (chloroform) to give a further quantity of trithiocarbonate (60 mg) and *trans*-2-(*NN*-diethylthiocarbamoylthio)cyclohexanol (26) (72 mg), b.p. 135° at 0.15 mmHg, ν_{\max} 3500 and 3330 cm^{-1} (Found: C, 53.55; H, 8.3; N, 5.5; S, 25.8%; M^+ , 247. $\text{C}_{11}\text{H}_{21}\text{NOS}_2$ requires C, 53.4; H, 8.55; N, 5.7; S, 25.9%; M , 247).

(iv) Reaction of 1,2-epoxycyclohexane (0.50 g) with the carbamate (1.12 g) in ethanol (35 ml) and water (15 ml) at ambient temperature for 24 h gave *trans*-2-(*NN*-diethylthiocarbamoylthio)cyclohexanol (1.24 g), identical (i.r. spectrum) with that obtained in the preceding experiment.

(v) Reaction of 2,3-epoxy-trans-decalin (1.0 g) and the carbamate (1.55 g) under the same conditions gave *3 α -(*NN*-diethylthiocarbamoylthio)-trans-decalin-2 β -ol* (2.25 g), an oil (purified by t.l.c. in ether), ν_{\max} 3550 and 3380 cm^{-1} (Found: C, 59.95; H, 9.0; N, 4.7; S, 21.5%; M^+ , 301. $\text{C}_{15}\text{H}_{27}\text{NOS}_2$ requires C, 59.75; H, 9.0; N, 4.6; S, 21.3%; M , 301).

DL-threo-2-(*NN*-Diethylthiocarbamoylthio)-1-methylpropyl Toluene-*p*-sulphonate (25).—Reaction of *DL*-threo-3-(*NN*-diethylthiocarbamoylthio)butan-2-ol (0.6 g) with toluene-*p*-sulphonyl chloride (1.6 g) in pyridine (7 ml) for 1 h at 0°,

followed by 24 h at ambient temperature, gave the crude derivative (0.32 g). Repeated treatment by t.l.c. (chloroform) failed to give analytically pure material, though the spectral characteristics were satisfactory: ν_{\max} 1380, 1358, and 1135 cm^{-1} , τ 2.5 (4H, m), 4.8—5.8 (2H, m), 5.8—6.8 (4H, m), 7.59 (3H, s), and 8.4—8.8 (12H, m) (Found: C, 52.65; H, 7.1; N, 3.3. Calc. for $\text{C}_{16}\text{H}_{25}\text{NO}_3\text{S}_2$: C, 51.2; H, 6.7; N, 3.7%).

A solution of this derivative (0.3 g) and potassium acetate (0.8 g) in ethanol (10 ml) was boiled under reflux for 15 h, then cooled, and poured into water. Extraction with chloroform and purification by t.l.c. (chloroform) gave, as the only recognisable product, the original dithiourethane (24) (70 mg) (i.r. spectrum).

trans-2-(*NN*-Diethylthiocarbamoylthio)cyclohexyl Toluene-*p*-sulphonate (27).—Under similar conditions, *trans*-2-(*NN*-diethylthiocarbamoylthio)cyclohexanol (0.5 g) and toluene-*p*-sulphonyl chloride (0.76 g) in pyridine (5 ml) likewise gave the crude derivative, which by t.l.c. (chloroform) afforded crystals, m.p. 102—103° (from ether), ν_{\max} 1140 and 1120 cm^{-1} , τ 2.5 (4H, m), 5.3—6.5 (6H, m), 7.60 (3H, s), 7.65—8.55 (8H, m), and 8.70 (6H, t); analytical purity could not be achieved (Found: C, 55.2; H, 7.05; N, 3.8. Calc. for $\text{C}_{18}\text{H}_{27}\text{NO}_3\text{S}_2$: C, 53.8; H, 6.8; N, 3.5%).

Solvolysis of this derivative (0.1 g) with potassium acetate (0.25 g) in boiling ethanol (5 ml) for 24 h gave only the original dithiourethane (26) (50 mg).

trans-2-(Phenylthiocarbamoylthio)cyclohexanol (28).—Phenyl isothiocyanate (2.08 g) in benzene (6 ml) was added slowly to a stirred solution of *trans*-2-mercaptocyclohexanol²¹ (2.07 g) and *NN*-diethylcyclohexylamine (0.2 g) in benzene (12 ml). After 24 h the mixture was concentrated to an oil, which crystallised on storage in benzene-petroleum at 0°. Recrystallisation from benzene gave the dithiocarbamate (3.8 g) as a solvate, m.p. 77—78° (Found: C, 62.9; H, 6.5; N, 4.2; S, 21.0. $\text{C}_{13}\text{H}_{17}\text{NOS}_2 \cdot 0.5\text{C}_6\text{H}_6$ requires C, 62.7; H, 6.6; N, 4.6; S, 20.9%). Recrystallisation from carbon tetrachloride gave the solvent-free compound, m.p. 98° (Found: C, 58.7; H, 6.3; S, 24.0. $\text{C}_{13}\text{H}_{17}\text{NOS}_2$ requires C, 58.4; H, 6.5; S, 24.0%).

Acetylation. A mixture of the dithiocarbamate (0.75 g), acetic anhydride (1.5 g), and pyridine (0.85 g) was heated on a steam-bath for 10 min and then set aside for 78 h. Addition of petroleum gave a solid (0.78 g) which was collected, washed with water, and dried. Recrystallisation from carbon tetrachloride and then from carbon tetrachloride-petroleum gave needles of *trans*-2-(phenylthiocarbamoylthio)cyclohexyl acetate (29) (0.28 g), m.p. 136°, ν_{\max} 1736 and 1046 cm^{-1} (Found: C, 57.9; H, 6.3; N, 4.2; S, 20.9. $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}_2$ requires C, 58.2; H, 6.2; N, 4.5; S, 20.7%).

Evaporation of the mother liquors, and repeated crystallisation of the residue from methanol, and finally from aqueous methanol, gave *trans*-2-(acetylthio)(phenylimino)methylthio)cyclohexyl acetate (30) (0.21 g), yellow needles, m.p. 92°, ν_{\max} 1733, 1702, 1066, and 1044 cm^{-1} (Found: C, 58.2; H, 6.2; N, 3.55; S, 18.2. $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}_2$ requires C, 58.1; H, 6.0; N, 3.95; S, 18.2%).

trans-2-Phenyliminoperhydro-1,3-benzoxathiolan (37).—(i) *trans*-2-(Phenylthiocarbamoylthio)cyclohexanol (1.2 g) was added in portions to thionyl chloride (7.2 g) at 0°; the solution was kept at 0° for 48 h and was then added to a stirred suspension of sodium hydrogen carbonate (27 g) in water (80 ml) at 0°. After 2 h a semisolid had been formed, and this was collected, washed with water, dried,

and extracted with boiling benzene. The extracts were concentrated and mixed with a solution of picric acid in benzene, whereupon a yellow crystalline precipitate was formed. Next day, this was collected and recrystallised from benzene to give the *picrate* of the phenylimino-compound (0.16 g), m.p. 174—176° (Found: C, 49.8; H, 4.0; N, 11.9. $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_8\text{S}$ requires C, 49.4; H, 3.9; N, 12.1%). The mother liquor was evaporated, and the residue was triturated with a mixture of water (10 ml) and 2-aminoethanol (3 ml) and extracted with ether. The extract was washed with aqueous 10% 2-aminoethanol and finally with water, and it was then dried and evaporated. Recrystallisation of the residue from chloroform-methanol afforded sulphur, m.p. 116° (Found: S, 100.2%).

Treatment of the *picrate* (93 mg) with aqueous 5% 2-aminoethanol (10 ml), followed by extraction with ether, gave the free *phenylimino-compound* (44 mg), m.p. 103° (from ether), ν_{\max} 1655 cm^{-1} , λ_{\max} 250 nm (ϵ 8000) (Found: C, 67.0; H, 6.4; N, 5.8; S, 14.0. $\text{C}_{13}\text{H}_{15}\text{NOS}$ requires C, 66.9; H, 6.5; N, 6.0; S, 13.7%).

(ii) Dropwise addition of a solution of toluene-*p*-sulphonyl chloride (0.20 g) in pyridine (1 ml) to *trans*-2-(phenylthiocarbamoylthio)cyclohexanol (0.27 g) in pyridine (1 ml) at 0°, followed by storage at ambient temperature for 48 h and dilution with water, gave a semi-solid, which was washed with water and then with boiling petroleum. Recrystallisation of the residue from ether-petroleum gave the same phenylimino-compound (53 mg), m.p. and mixed m.p. 103°.

Benzyl trans-2-Hydroxycyclohexyl Sulphoxide.—A mixture of *trans*-2-benzylthiocyclohexanol²² (4.4 g), sodium periodate (4.5 g), water (110 ml), and dioxan (35 ml) was stirred for 4 h. The solid (0.7 g) which had separated was collected, washed with water, and recrystallised from chloroform-ether to give *isomer A* of the sulphoxide, m.p. 155°, ν_{\max} 3400 and 1053 cm^{-1} (Found: C, 65.5; H, 7.4; S, 13.7. $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$ requires C, 65.5; H, 7.6; S, 13.45%).

The aqueous filtrate was extracted with chloroform to give a solid mixture (3.8 g), m.p. 115—140°, which by fractional crystallisation from chloroform-ether gave *isomer A*, m.p. 155°, and *isomer B*, m.p. 128°, ν_{\max} 3425, 1083, and 1022 cm^{-1} (Found: C, 65.5; H, 7.4; S, 13.7%).

Benzyl trans-2-Hydroxycyclohexyl Sulphone (32).—(i) Treatment of benzyl *trans*-2-hydroxycyclohexyl sulphide (4.7 g) with 30% hydrogen peroxide (12 ml) in acetic acid (15 ml) on a steam-bath for 4 h, followed by evaporation to dryness, gave a solid residue (5.2 g), m.p. 120—121°, which on recrystallisation once from ether afforded the *sulphone*, m.p. 122°, ν_{\max} 3520, 1318, and 1126 cm^{-1} (Found: C, 61.0; H, 7.3; S, 12.6. $\text{C}_{13}\text{H}_{18}\text{O}_3\text{S}$ requires C, 61.4; H, 7.1; S, 12.6%).

(ii) Similar treatment of a mixture (0.55 g) of isomers A and B of the sulphoxide gave the *sulphone* (0.53 g), m.p. and mixed m.p. 122°.

trans-2-Benzylsulphonylcyclohexyl Toluene-*p*-sulphonate (33).—Reaction of the *sulphone* (32) (5.2 g) with toluene-*p*-sulphonyl chloride (6.0 g) in pyridine (12 ml) at 0° for 72 h gave the toluene-*p*-sulphonate, m.p. 141—143° (from methanol), ν_{\max} 1380, 1322, and 1156 cm^{-1} (Found: C, 58.5; H, 6.1; S, 16.0. $\text{C}_{20}\text{H}_{24}\text{O}_5\text{S}_2$ requires C, 58.8; H, 5.9; S, 15.7%).

cis-2-Benzoylthiocyclohexyl Benzyl Sulphone (39).—(i) A

²¹ C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 1949, 278.

²² C. D. Nenitzescu and N. Scărlătescu, *Ber.*, 1935, 68, 587.

solution of the toluene-*p*-sulphonate (33) (0.8 g) and potassium thiobenzoate (1.8 g) in dimethylformamide (15 ml) was boiled under reflux for 4 h, under nitrogen, and then set aside overnight. Removal of most of the solvent, followed by dilution with water and extraction with chloroform, gave an oil (0.55 g) which was dissolved in benzene-petroleum and stored at 0° for 120 h. The deposited solid was collected and recrystallised from benzene-petroleum to give *benzyl cyclohex-2-enyl sulphone* (38) (26 mg), m.p. 98°, ν_{\max} 1650, 1321, and 1130 cm^{-1} , τ 2.60 (5H, s, Ph), 4.0 (2H, m, CH=CH), 5.79 (2H, s, CH₂Ar), 6.4 (1H, m, CH·SO₂), and 7.7–8.5 (6H, m, alicyclic) (Found: C, 66.2; H, 6.7; S, 13.7. C₁₃H₁₆O₂S requires C, 66.0; H, 6.4; S, 13.6%).

(ii) The toluene-*p*-sulphonate (0.6 g), potassium thiobenzoate (1.4 g), and ethanol (15 ml) were boiled together for 24 h under nitrogen. Evaporation, dilution of the

residue with water, and extraction with ether gave an oil, which solidified on treatment with benzene-petroleum. This solid was dissolved in methanol and stored at 0°; a few crystals of the unsaturated sulphone, m.p. and mixed m.p. 98°, were deposited. The mother liquor was evaporated and the residue was recrystallised from ether to give *cis-2-benzoylthiocyclohexyl benzyl sulphone* (39) (0.21 g), m.p. 105°, ν_{\max} 1661, 1330, and 1123 cm^{-1} (Found: C, 64.0; H, 6.0; S, 17.2. C₂₀H₂₂O₃S₂ requires C, 64.1; H, 5.9; S, 17.1%).

Reduction of this thiobenzoate (80 mg) with lithium aluminium hydride (0.4 g) in boiling tetrahydrofuran for 48 h gave an oil, ν_{\max} 1312 and 1135 cm^{-1} (sulphone still present).

We thank the Nuffield Foundation for a Fellowship (to M. E. A.).

[4/2185 Received, 23rd October, 1974]