

Dithiols. Part XXVII.¹ Conversion of Aliphatic and Alicyclic Carbonates and Thiocarbonates into Trithiocarbonates

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Reaction of the carbonates of ethane-1,2-, propane-1,2-, *meso*-butane-2,3-, DL-butane-2,3-, and cyclohexane-*cis*-1,2-diol with sodium (or potassium) *O*-ethyl xanthate gave the corresponding trithiocarbonates with (when detectable) a net inversion of configuration at one of the carbon atoms concerned; better yields were obtained from thiocarbonates. The carbonate and the thiocarbonate from cyclohexane-*trans*-1,2-diol reacted by a different mechanism and gave the *trans*-trithiocarbonate. High yields of trithiocarbonates were obtained, with retention of configuration, from several dithiocarbonates. Reactions on carbonate, thiocarbonate, and dithiocarbonate analogues in the *trans*-decalin system proceeded less readily. The transformations into trithiocarbonates involve various mechanisms, some of which require attack on the carbonyl (or thiocarbonyl) carbon atom: others proceed with attack on the 'alkyl' carbon atom of the cyclic ester.

Mass spectral and i.r. parameters for some cyclic thiocarbonates are tabulated, and the significance of the low-frequency bands is discussed.

NUCLEOPHILIC attack by alcohols or amines on the carbonyl carbon atom in a cyclic carbonate, to give ring-opened products, is well known.^{2,3} Methyl 4,6-*O*-benzylidene- α -D-glucopyranoside 2,3-carbonate (1) and 2,3-thiocarbonate (2) are attacked at the carbonyl or the thiocarbonyl carbon atom by these types of nucleophiles and also by toluene- α -thiol.³ However, under more vigorous conditions ethylene carbonate is an efficient hydroxyethylating agent in its reactions with phenoxide and thiolate anions,⁴ an indication that the ester is susceptible also to attack at the 'alkyl' carbon atom, and the reactions of ethylene thiocarbonate with alkyl halides and with halide ions⁵ likewise involve this type of fission. Furthermore, Searles, Hays, and Lutz

found that cyclic carbonates of 1,2- and of 1,3-diols gave thiirans⁶ and thietans,⁷ respectively, on reaction with alkali thiocyanates, and the fact that the episulphide derived in this way from the carbonate of *meso*-butane-2,3-diol also had the *meso*-configuration was consistent with attack at the 'alkyl' position, as was their observation that the yields of episulphides diminished with increased substitution on the 'alkyl' carbon atoms.* Steric hindrance is probably also the reason for the absence of attack by thiolate anion on the sugar ring carbon atoms in the derivatives (1) and (2).

Thiirans react with xanthates to give cyclic trithiocarbonates,^{9,10} and it therefore seemed likely that trithiocarbonates could be obtained in one operation

* A route can be formulated from a cyclic carbonate to an episulphide *via* an epoxide, involving initial attack on the carbonyl carbon atom, but the carbonate of *meso*-butane-2,3-diol should then have given the DL-epoxide and thence, by the usual mechanism⁸ the DL-episulphide; the stereochemical evidence thus rules out this possibility.

¹ M. E. Ali, N. G. Kardouche, and L. N. Owen, preceding paper.

² B. J. Ludwig and E. C. Piech, *J. Amer. Chem. Soc.*, 1951, **73**, 5779; M. M. Baizer, J. R. Clark, and J. Swidinsky, *J. Org. Chem.*, 1957, **22**, 1595; M. M. Baizer, J. R. Clark, and E. Smith, *ibid.*, p. 1706; J. Katzhendler, I. Ringel, and S. Sarel, *J.C.S. Perkin II*, 1972, 2019; E. I. Stout, W. M. Doane, and K. E. Kolb, *J. Org. Chem.*, 1971, **36**, 3126.

³ W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohydrate Res.*, 1969, **11**, 321.

⁴ M. S. Morgan and L. H. Cretcher, *J. Amer. Chem. Soc.*, 1946, **68**, 781; W. W. Carlson and L. H. Cretcher, *ibid.*, 1947, **69**, 1952; U.S.P. 2,448,767 (*Chem. Abs.*, 1949, **43**, 673).

⁵ F. N. Jones and S. Andreades, *J. Org. Chem.*, 1969, **34**, 3011.

⁶ S. Searles, H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, 1962, **27**, 2832.

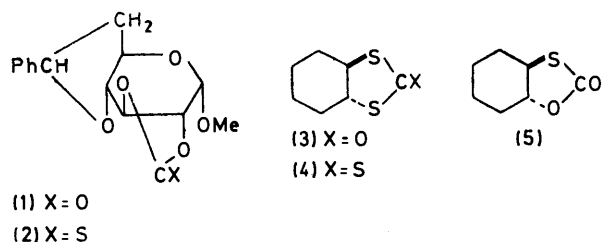
⁷ S. Searles, H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, 1962, **27**, 2828.

⁸ M. G. Ettlinger, *J. Amer. Chem. Soc.*, 1950, **72**, 4792; E. E. van Tamelen, *ibid.*, 1951, **73**, 3444; C. C. Price and P. F. Kirk, *ibid.*, 1953, **75**, 2396.

⁹ C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, 1946, 1050; A. M. Creighton and L. N. Owen, *ibid.*, 1960, 1024; L. D. Hall, L. Hough, and R. A. Pritchard, *ibid.*, 1961, 1537.

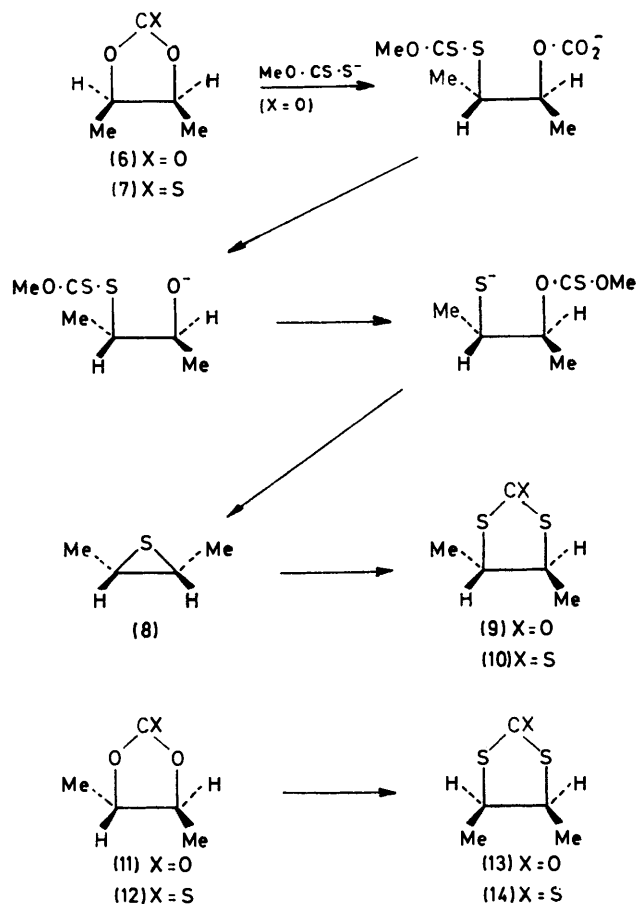
¹⁰ S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1960, 1030.

by treatment of a cyclic carbonate with the salt of an *O*-alkyl xanthate. If so, this would provide a simple process for the conversion of a vicinal diol into a dithiol,



because the latter type of compound can be obtained by reductive cleavage of a cyclic trithiocarbonate.¹⁰ Meloy¹¹ has reported the formation of the *trans*-trithiocarbonate (4) by reaction of the cyclic thiolcarbonate (5) with potassium *O*-methyl xanthate.

Ethylene carbonate reacted with sodium *O*-methyl, *O*-ethyl, *O*-propyl, and *O*-butyl xanthate, in the corresponding alcohol at reflux temperature, to give ethylene



SCHEME 1 Where chiral forms are shown, racemic forms are to be understood

trithiocarbonate in yields of 22, 25, 50, and 25%, respectively. Propylene carbonate, with sodium *O*-ethyl xanthate, gave propylene trithiocarbonate (18%). The

carbonate (6) of *meso*-butane-2,3-diol afforded the DL-trithiocarbonate (10) (18%) in accord with the expectation that attack by xanthate would lead initially to the *meso*-episulphide (8), the subsequent reaction of which would proceed¹ with inversion at one carbon atom (Scheme 1). In a similar way the DL-carbonate (11) gave the *meso*-trithiocarbonate (14) (34%). The stereoisomers (10) and (14), which have almost identical m.p.s, are readily identified by their n.m.r. spectra,¹² and their i.r. spectra also show small but significant differences.

The rather low yields of trithiocarbonates obtained in these reactions can be attributed to competitive attack on the carbonyl carbon atom, which leads to loss of substrate *via* the intermediates (15) and (16); the latter, being a mixed anhydride, is probably easily solvolysed to give the diol. Because a thiocarbonyl group is less susceptible to nucleophilic attack we therefore prepared the two thioncarbonates (7) and (12) by reaction of the appropriate diols with thiocarbonyl chloride; treatment of these derivatives with xanthate then gave the trithiocarbonates (10) and (14) in yields of 77 and 73%, respectively. The effect of increased substitution was revealed by the finding that the carbonate and the thioncarbonate of 2-methylbutane-2,3-diol gave yields of only 12 and 15%, respectively, of the corresponding trithiocarbonate.

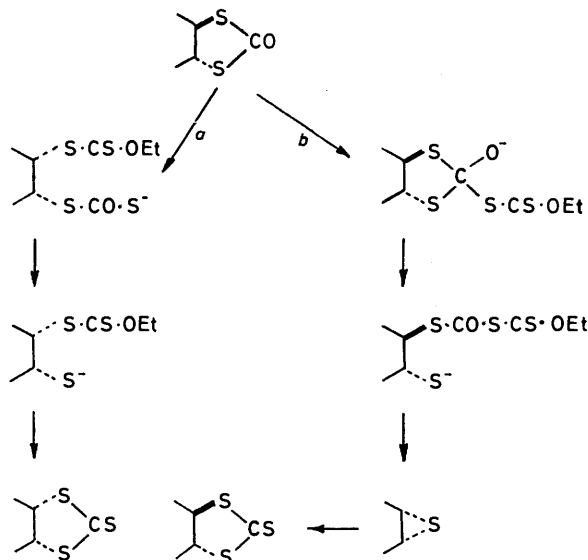
Reaction of the two trithiocarbonates (10) and (14) with mercury(II) acetate gave the dithiolcarbonates (9) and (13), each of which on treatment with xanthate was converted back into the corresponding trithiocarbonate in almost theoretical yield. Attack by xanthate at the 'alkyl' position, with inversion of configuration, followed by loss of carbonyl oxysulphide, and cyclisation, would have given a trithiocarbonate of opposite configuration (Scheme 2, route *a*); fission of the C-S bond by intermolecular attack must therefore be difficult, and is completely overshadowed by attack on the carbonyl group (route *b*), which leads, *via* the episulphide, to the trithiocarbonate of the observed configuration.

On treatment with xanthate, the carbonate (17) and the thioncarbonate (18), both prepared from cyclohexane-*cis*-1,2-diol, gave the *trans*-trithiocarbonate (4) in yields of 29 and 60%, respectively, the stereochemical result thus being the same as that observed with the *meso*-butane-2,3-diol derivatives (6) and (7), and an improved yield from the thioncarbonate again being evident. However, the *trans*-compounds (19) and (20) also gave the *trans*-trithiocarbonate (4), though with yields of only 12 and 5% respectively, clearly by a different mechanism. This contrast between the behaviour of the aliphatic and the alicyclic DL-carbonates arises simply because the normal mechanism (Scheme 1), when applied to the *trans*-esters (19) and (20), would require the formation, as an intermediate, of the non-

¹¹ C. R. Meloy, *Trans. Illinois State Acad. Sci.*, 1963, **56**, 146.

¹² C. G. Overberger and A. Drucker, *J. Org. Chem.*, 1964, **29**, 360.

existent *trans*-1,2-epithiocyclohexane. Attack on the 'alkyl' position, which no doubt occurs to a considerable extent, is therefore non-productive of *cis*-trithiocarbonate, and the formation of the *trans*-compound (4) must arise because of attack at the



SCHEME 2

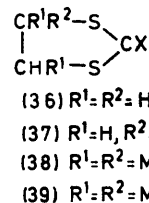
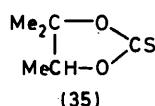
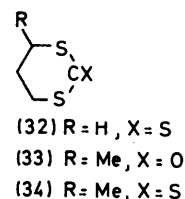
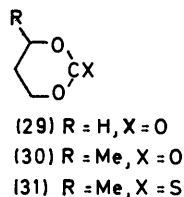
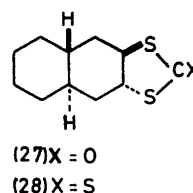
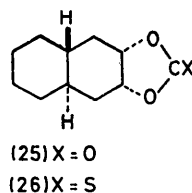
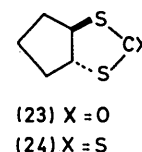
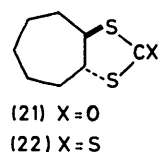
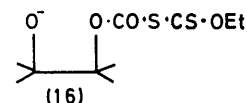
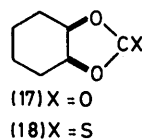
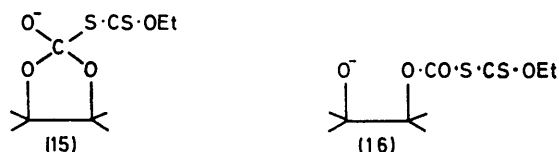
carbonyl or thiocarbonyl group to give intermediates analogous to (16) (in the *trans*-configuration), which, amongst other reactions, can form some 1,2-epoxycyclohexane, and thence the trithiocarbonate (4). This mechanism is supported by the lower yield here afforded by the thioncarbonate.

The *trans*-dithiolcarbonate (3) and the cycloheptane analogue (21) gave, almost quantitatively, the *trans*-trithiocarbonates (4) and (22) respectively, but the cyclopentane compound (23) gave only a trace of the trithiocarbonate (24). The use of sodium *NN*-diethyl-dithiocarbamate (which converts epoxides into trithiocarbonates)¹ instead of xanthate, in a reaction on the dithiolcarbonate (3), gave only a poor yield (15%) of the trithiocarbonate (4).

Reaction of *trans*-decalin-2 α ,3 α -diol with diethyl carbonate and with thiocarbonyl chloride afforded the cyclic carbonate (25) and the thioncarbonate (26), but *trans*-decalin-2 β ,3 α -diol failed to give the corresponding *trans*-fused esters (which would require the cyclohexane ring involved to assume a boat conformation). On treatment with sodium ethyl xanthate the carbonate (25) gave mainly the 2 α ,3 α -diol (attack on the carbonyl function); in contrast to the case of the cyclohexane analogue (17) no trithiocarbonate was formed, and only a small amount (5%) was obtained from the thioncarbonate (26). The 2 β ,3 α -dithiolcarbonate (27), prepared from the pure trithiocarbonate¹ by reaction with mercury(II) acetate, afforded a better yield (51%) but although the i.r. spectra of these products were essentially identical with that of the known¹ compound (28) the m.p.s were not sharp, and the presence of an

isomeric trithiocarbonate cannot be excluded; attempts to effect separation by t.l.c. and by fractional crystallisation from a variety of solvents were unsuccessful.

The marked contrast between the reactions of the cyclohexane and the *trans*-decalin derivatives is no doubt due to the relative lack of conformational mobility in the latter system. This restriction applies also to the *trans*-fused 4,6-benzylidene derivative (1), but because attack on the carbonyl carbon atom in this glucoside is favoured,³ the formation of a trithiocarbonate [by the mechanism suggested for the reaction of the *trans*-carbonate (19) with xanthate] was thought to be a



possibility. However, none was obtained. If the configuration at C-4 in the sugar derivative (1) is inverted, the stereochemistry becomes analogous to that of a

cis-decalin system and the conformational restraints are less severe.¹³ We therefore synthesised the *galacto*-analogue of (1) from methyl 4,6-*O*-benzylidene- α -D-galactoside, but, as in the case of the *gluco*-compound, reaction with xanthate merely resulted in de-esterification.

Prolonged treatment of the cyclic carbonate (29) of propane-1,3-diol with potassium ethyl xanthate in boiling ethanol gave a trace of trimethylene trithiocarbonate (32). Separate treatment of the intermediate trimethylene sulphide, under the same conditions, likewise gave only a trace of the same product; under milder conditions¹⁰ no trithiocarbonate had been detected. There is clearly an enormous difference between the reactivities of the thietan and the thiiran systems towards this reagent. The carbonate (30) of butane-1,3-diol likewise gave only a trace of the corresponding trithiocarbonate (34).

The reported isomerisation of 1,2-thiocarbonyldioxyethane to 1,2-carbonyloxythioethane, by reaction with potassium iodide,⁵ prompted us to examine an alicyclic analogue, but neither *cis*- nor *trans*-1,2-thiocarbonyldioxycyclohexane was affected by such treatment.

Mass Spectrometry of Cyclic Thiocarbonates.—Previous studies on the mass spectrometry of carbonate and thiocarbonate esters have been restricted almost entirely to acyclic compounds;¹⁴ only three cyclic carbonates have been examined.¹⁵ That of butane-2,3-diol (configuration not specified) showed an abundant molecular ion peak and ions ($M - 44$) corresponding to loss of carbon dioxide accompanied by migration of hydrogen or of a methyl group. Similarly, the main fragmentation of *cis*- and of *trans*-1,2-carbonyldioxycyclohexane involved loss of carbon dioxide (*a*) with hydrogen migration (to give the cyclohexanone radical ion), and (*b*) with ring contraction (to give formylcyclopentane radical ion). Route (*a*) then led by known processes to further ions, including the cyclohexenyl cation, and route (*b*) produced, amongst other products, the cyclopentyl cation.

Apart from a brief mention of the mass spectrum of ethylene thioncarbonate,⁵ cyclic thiocarbonates have apparently never been examined, and the results of low-resolution measurements on some of our compounds of this type are summarised in Table I. In the absence of confirmatory evidence from accurate mass measurements, *etc.*, the detailed fragmentation patterns which

have been suggested elsewhere¹⁶ are tentative, though in many respects they are analogous to those established¹⁵ for the cyclic carbonates.

All the cyclic thiocarbonates showed molecular ion peaks, and all formed fragments by loss of COS or CS₂; three dithiolcarbonates also showed peaks at $M - CO$. The trithiocarbonates (24), (4), (22), and (28) showed the ions $M - CS_2 - SH$, and the carbonyldithio-compounds (23), (3), (21), and (27) showed the ions $M - COS - SH$; these were probably the cycloalkenyl cations, which formed the base peaks in all except the spectra of the two decalin derivatives. Fairly abundant ions of one mass unit less (the cycloalkenyl radical ions) were also evident in all eight spectra. The lower cycloalkyl cations (*e.g.* cyclopentyl from the cyclohexane compounds) were *not* observed. The aliphatic trithiocarbonate (34), also, showed an ion $M - CS_2 - SH$ which was probably a butenyl cation; an ion having the mass of the corresponding radical ion was also formed.

The thioncarbonates (18) and (20) showed the ions $M - COS - OH$, probably again the cycloalkenyl cations (the surprising difference in relative abundance between the two stereoisomers was confirmed by repeating the fragmentations on fresh samples), but only weak peaks for the radical ion $M - COS - H_2O$. In contrast, the decalin analogue (26) gave no fragment $M - COS - OH$ at *m/e* 135 but an abundant radical ion at *m/e* 134, which was also abundant in the spectrum of the corresponding carbonate (see Experimental section). Of special interest is the strong peak at *m/e* 69 in the spectra of the *cis*- and the *trans*-thioncarbonate (18) and (20), which can be attributed to the same cyclopentyl cation as that produced¹⁵ from the corresponding cyclic carbonates.

Infrared Spectra of Cyclic Thiocarbonates.—The i.r. spectra of several cyclic trithiocarbonates have been measured previously^{5,10,12,17,18} but the published information has usually been restricted to the absorption bands in the 1000–1100 cm⁻¹ region, characteristic of the C=S stretching mode. In only one instance¹⁸ has any special reference been made to the strong bands in the 800–900 cm⁻¹ region; in ethylene trithiocarbonate these were attributed to the C-S function, the higher frequency (*cf.* the normal values of 600–700 cm⁻¹) and much greater intensity being due to the proximity of the thione function. Strong absorption in the 800–900 cm⁻¹ region is also shown by acyclic trithiocarbonates,^{19,20} and by cyclic^{5,12,18,21} and acyclic^{19,22,23} dithiolcarbonates; in the last class, the absorption is said²² to result from asymmetric S-C-S stretching.

All our five-membered cyclic trithiocarbonates and

¹³ M. V. Jesudason and L. N. Owen, *J.C.S. Perkin I*, 1974, 2019.

¹⁴ P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 2469; J. B. Thomson, P. Brown, and C. Djerassi, *ibid.*, p. 4049.

¹⁵ P. Brown and C. Djerassi, *Tetrahedron*, 1968, **24**, 2949.

¹⁶ N. G. Kardouche, Ph.D. Thesis, University of London, 1974.

¹⁷ R. Mecke, R. Mecke, and A. Lüttringhaus, *Z. Naturforsch.*, 1955, **10b**, 367; R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 1955, 2901; J. I. Jones, W. Kynaston, and J. L. Hales, *ibid.*, 1957, 614; K. Takeda, T. Komeno, J. Kawanami, S. Ishihara, H. Kadokawa, H. Tokura, and H. Itani, *Tetrahedron*, 1965, **21**, 329; D. A. Lightner and C. Djerassi, *ibid.*, p. 583; A. K. M. Anisuzzaman and L. N. Owen, *J. Chem. Soc. (C)*, 1967, 1021; S. Hayashi, M. Furukawa, Y. Fujino, T. Nakao, and K. Nagato, *Chem. and Pharm. Bull. (Japan)*, 1971, **19**, 1594.

¹⁸ R. Mecke, R. Mecke, and A. Lüttringhaus, *Chem. Ber.*, 1957, **90**, 975.

¹⁹ L. H. Little, G. W. Poling, and J. Leda, *Canad. J. Chem.*, 1961, **39**, 745.

²⁰ B. Krebs and A. Müller, *Z. anorg. Chem.*, 1966, **348**, 107.

²¹ E. J. Corey and R. B. Mitra, *J. Amer. Chem. Soc.*, 1962, **84**, 2938.

²² R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, 1961, **17**, 679.

²³ T. Taguchi and M. Nakao, *Tetrahedron*, 1962, **18**, 245.

dithiolcarbonates showed strong absorption between 860 and 900 cm^{-1} (Table 2); however, the two six-membered cyclic trithiocarbonates (32) and (34) showed negligible absorption in this region, though the six-membered cyclic dithiolcarbonate (33) gave a strong

only slightly greater than this. Assignments of bands in this region should evidently be undertaken with caution, a view also expressed elsewhere²⁰ and reinforced by the fact that very strong absorption at 850 cm^{-1} is shown by diethyl carbonate.²¹ Bands at

TABLE I
Mass spectral data^a

Trithiocarbonates

trans-1,2-Thiocarbonyldithiocyclopentane (24)

<i>m/e</i>	176 ^b	100 ^c	85	76	71	67 ^d	66 ^e	65	45	41
%	40	20	22	58	17	100	20	7	17	27

trans-1,2-Thiocarbonyldithiocyclohexane (4)

<i>m/e</i>	190 ^b	114 ^c	99	82	81 ^d	80 ^e	79	76	73	54	45	44	41
%	61	5	50	13	100	59	23	36	41	29	27	24	40

trans-1,2-Thiocarbonyldithiocycloheptane (22)

<i>m/e</i>	204 ^b	128 ^c	95 ^d	94 ^e	86	85	81	79	76	73	71	68	67
%	74	7	100	25	12	12	38	36	22	11	11	27	51
<i>m/e</i>	66	65	60	55	54	53	45	41					
%	9	9	11	29	25	18	20	42					

2 β ,3 α -Thiocarbonyldithio-*trans*-decalin (28)

<i>m/e</i>	244 ^b	168 ^c	135 ^d	134 ^e	121	119	99	96	95	94	93	92	91
%	100	5	43	36	61	9	11	16	73	13	25	23	25
<i>m/e</i>	81	79	76	67	55	41							
%	19	30	14	43	20	34							

1,3-Thiocarbonyldithiobutane (34)

<i>m/e</i>	164 ^b	120 ^f	88 ^c	76	73	60	59	55 ^g	54 ^h	53	47	46	45
%	100	35	7	37	13	48	13	65	15	5	17	43	24
<i>m/e</i>	44	43	42	41									
%	15	8	6	17									

Dithiolcarbonates

trans-1,2-Carbonyldithiocyclopentane (23)

<i>m/e</i>	160 ^b	100 ⁱ	85	71	67 ^d	66 ^e	65	45	41
%	25	61	25	24	100	18	12	21	20

trans-1,2-Carbonyldithiocyclohexane (3)

<i>m/e</i>	174 ^b	146 ^j	114 ⁱ	82	81 ^d	80 ^e	79	73	67	54	45	44	41
%	26	12	26	9	100	46	26	46	38	15	30	15	35

trans-1,2-Carbonyldithiocycloheptane (21)

<i>m/e</i>	188 ^b	160 ^j	128 ⁱ	95 ^d	94 ^e	86	85	81	79	73	71	68	67
%	39	26	15	100	32	20	23	40	47	18	18	26	60
<i>m/e</i>	66	65	60	55	54	53	45	41					
%	12	12	17	32	17	20	44	53					

2 β ,3 α -Carbonyldithio-*trans*-decalin (27)

<i>m/e</i>	228 ^b	200 ^j	168 ⁱ	135 ^d	134 ^e	121	119	99	96	95	94	93	92
%	46	6	15	30	24	100	9	9	17	65	11	20	17
<i>m/e</i>	91	81	79	67	55	41							
%	17	17	22	35	13	26							

Thioncarbonates

cis-1,2-Thiocarbonyldioxycyclohexane (18)

<i>m/e</i>	158 ^b	98 ⁱ	81 ^d	80 ^e	79	69 ^k	67	57	55	54	41
%	78	5	100	7	15	37	12	18	37	28	70

trans-1,2-Thiocarbonyldioxycyclohexane (20)

<i>m/e</i>	158 ^b	98 ⁱ	81 ^d	80 ^e	79	69 ^k	67	57	55	54	41
%	44	8	9	5	5	77	10	38	31	17	100

2 α ,3 α -Thiocarbonyldioxy-*trans*-decalin (26)

<i>m/e</i>	212 ^b	152 ⁱ	134 ^e	119	109	108	95	94	92	91	81	79	70
%	73	5	84	5	5	5	28	28	37	9	54	35	5
<i>m/e</i>	68	67	57	55	41								
%	14	100	13	35	46								

^a Ions of *m/e* < 40 or % < 5 are omitted. ^b *M*⁺. ^c *M* - CS₂. ^d Cycloalkenyl cation. ^e Cycloalkenyl radical ion. ^f *M* - CS. ^g Butenyl cation. ^h Butenyl radical ion. ⁱ *M* - COS. ^j *M* - CO. ^k Cyclopentyl cation.

band at 902 cm^{-1} . In the light of these results on compounds all containing the S-C-S function, it was surprising to find that the thioncarbonate (20) gave a strong peak at 898 cm^{-1} ; some of the other thioncarbonates showed strong absorption at frequencies

1303 and 1368 cm^{-1} shown by ethylene thioncarbonate⁵ and at 1282 cm^{-1} by some carbohydrate thioncarbonates²⁴ have been attributed to the C=S function, though

²⁴ E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Carbohydrate Res.*, 1967, **3**, 354.

in 1,2:5,6-di-*O*-isopropylidene-3,4-*O*-thiocarbonyl-*D*-mannitol the origin of bands at 1300 and 1325 cm^{-1} is said²⁵ to be the C-O-C function in the ester group. All our thioncarbonates showed intense absorption in the 1270—1295 cm^{-1} region, but the bands between 1300 and 1365 cm^{-1} were also very strong.

TABLE 2

I.r. absorption maxima (in chloroform) (cm^{-1})	
Trithiocarbonates (1150—800 cm^{-1} region)	
(36)	1065, 950, 890, 836
(37)	1085, 1055, 878
(10)	1095, 1050, 995, 880
(14)	1099, 1075, 1000, 879
(39)	1080, 1055, 1005, 882
(24)	1098, 1060, 990, 862
(4)	1110, 1072, 1000, 875
(22)	1105, 1060, 995, 898, 870
(28)	1110, 1060, 875
(32)	1100, 1020, 935
(34)	1070, 1010, 940
Dithiolcarbonates (1700—1600 and 975—800 cm^{-1} regions) *	
(9)	1640, 865
(13)	1630, 862
(38)	1640, 885
(23)	1685, 1645, 875
(3)	1650, 1610, 870
(21)	1630, 895, 860
(33)	1600, 957, 902
Thioncarbonates (1400—800 cm^{-1} region)	
(7)	1365, 1320, 1280, 1140, 1050, 1030, 918
(12)	1345, 1322, 1282, 1175, 1030, 920
(35)	1362, 1308, 1278, 1140, 1098, 918, 890
(18)	1350, 1310, 1290, 1165, 1140, 970, 915
(20)	1350, 1322, 1295, 1185, 1155, 1105, 1020, 898
(26)	1340, 1310, 1285, 1150, 970
(31)	1362, 1270, 1205, 1082

* All the five-membered cyclic dithiolcarbonates showed maxima in the 1780—1710 cm^{-1} region, presumably overtones of the low-frequency bands.

EXPERIMENTAL

For general notes see preceding paper.

meso-2,3-Thiocarbonyldioxybutane (7).—A solution of thiocarbonyl chloride (12.7 g) in benzene (150 ml) was added to a mixture of *meso*-butane-2,3-diol²⁶ (5.0 g), pyridine (32 g), and benzene (150 ml), which was then stirred for 15 h and filtered. The filtrate was washed successively with water, 2*N*-hydrochloric acid, and water, then dried and evaporated to an oil, which on distillation gave a main fraction, b.p. 96—103° at 0.5 mmHg. This was purified by t.l.c. (benzene) and finally distilled to give the *thioncarbonate* (4.3 g), b.p. 76—77° at 0.2 mmHg, τ 4.94 (2H, m) and 8.55 (6H, m) (Found: C, 45.3; H, 6.0; S, 24.3. $\text{C}_5\text{H}_8\text{O}_2\text{S}$ requires C, 45.4; H, 6.1; S, 24.25%).

DL-2,3-Thiocarbonyldioxybutane (12).—DL-Butane-2,3-diol²⁷ (5.0 g) treated in the same way, gave the *thioncarbonate* (5.4 g), b.p. 79—80° at 0.2 mmHg, τ 5.38 (2H, m) and 8.44 (6H, m) (Found: C, 45.5; H, 6.0; S, 24.1%).

1,3-Thiocarbonyldioxybutane (31).—Treatment of butane-1,3-diol (5.0 g) with the same quantities of reagents as used with the butane-2,3-diols gave the *thioncarbonate* (0.6 g), m.p. 41° (from ether) (Found: C, 45.35; H, 6.0; S, 24.5%).

2-Methyl-2,3-thiocarbonyldioxybutane (35).—Similar re-

²⁵ B. R. Baker and H. S. Sachdev, *J. Org. Chem.*, 1963, **28**, 2135.

²⁶ F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 747.

²⁷ C. E. Wilson and H. J. Lucas, *J. Amer. Chem. Soc.*, 1936, **58**, 2396.

action of 2-methylbutane-2,3-diol²⁸ (3.5 g) with thiocarbonyl chloride (7.65 g) and pyridine (19 g) in benzene (180 ml) gave (t.l.c. first in chloroform, then in ether) the *thioncarbonate* (2.25 g), b.p. 81° at 0.3 mmHg (Found: C, 50.1; H, 6.8; S, 21.5. $\text{C}_6\text{H}_{10}\text{O}_2\text{S}$ requires C, 49.3; H, 6.9; S, 21.9%).

cis-1,2-Thiocarbonyldioxy-cyclohexane (18).—From cyclohexane-*cis*-1,2-diol²⁹ (6.0 g), thiocarbonyl chloride (12 g), pyridine (31 g), and benzene (300 ml), the crude product was purified first by column chromatography (benzene) and then by recrystallisation from benzene-petroleum to give the *thioncarbonate* (4.0 g), m.p. 30° (Found: C, 53.4; H, 6.4; S, 20.2. $\text{C}_7\text{H}_{10}\text{O}_2\text{S}$ requires C, 53.15; H, 6.4; S, 20.2%).

2 α ,3 α -Thiocarbonyldioxy-*trans*-decalin (26).—*trans*-Decalin-2 α ,3 α -diol³⁰ (1.7 g), thiocarbonyl chloride (2.3 g), pyridine (6 g), and benzene (350 ml) similarly gave the *thioncarbonate* (0.11 g), which after t.l.c. (chloroform) and recrystallisation from ether-petroleum had m.p. 111—112° (Found: C, 62.1; H, 7.6; S, 15.4. $\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}$ requires C, 62.2; H, 7.6; S, 15.1%).

cis-1,2-Carbonyldioxy-cyclohexane (17).—A stream of gaseous carbonyl chloride was passed for 30 min into a stirred solution of cyclohexane-*cis*-1,2-diol (7.5 g) and pyridine (8.4 g) in chloroform (50 ml) at 0°. The mixture was stirred at 0° for a further 30 min, and then for 1 h at ambient temperature before being washed with water. Evaporation of the dried solution and distillation of the residual oil gave the *carbonate* (5.3 g), b.p. 99° at 0.5 mmHg, which solidified, and had m.p. 38—39° (from petroleum) (Found: C, 59.2; H, 7.0. $\text{C}_7\text{H}_{10}\text{O}_3$ requires C, 59.1; H, 7.1%). The compound has been made previously,¹⁵ but no analysis or physical constants were recorded.

trans-1,2-Carbonyldioxy-cyclohexane (19).—By a similar procedure, except that toluene (150 ml) was used instead of chloroform, cyclohexane-*trans*-1,2-diol (5.0 g) gave the *carbonate* (3.0 g), m.p. 53—54° (lit.,³¹ 54—55°).

2 α ,3 α -Carbonyldioxy-*trans*-decalin (25).—Sodium (5 mg) was added to a mixture of *trans*-decalin-2 α ,3 α -diol (1.7 g) and diethyl carbonate (1.3 g), which was then heated to 180°, ethanol being collected by distillation. When no more was being formed, the residue was cooled and dissolved in benzene; the solution was washed, dried, and evaporated to give the *carbonate* (1.7 g), m.p. 121—122° (from ether), *m/e* 196 (M^+ , 9%), 152 (33), 134 (58), 121 (26), 119 (14), 109 (28), 108 (31), 98 (100), 96 (82), 95 (61), 94 (33), 93 (28), 92 (28), 91 (30), 81 (74), 79 (42), 70 (28), 68 (21), 67 (70), 57 (30), 55 (51), 41 (12), and 39 (35) (Found: C, 67.5; H, 8.4. $\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C, 67.3; H, 8.2%).

trans-1,2-Thiocarbonyldithiocycloheptane (22).—When the reaction of sodium (2.3 g) with ethanol (100 ml) was complete, 1,2-epoxycycloheptane³² (1.1 g) and carbon disulphide (10 g) were added, and the solution was boiled under reflux for 17 h, then cooled, diluted with water, and extracted with chloroform to give the *trithiocarbonate* (1.9 g), bright yellow crystals, m.p. 67—68° (from ether-petroleum) (Found: C, 47.2; H, 5.95; S, 47.0. $\text{C}_8\text{H}_{12}\text{S}_3$ requires C, 47.0; H, 5.9; S, 47.1%).

trans-1,2-Carbonyldithiocycloheptane (21).—A suspension

²⁸ N. A. Milas and S. Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302.

²⁹ M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 1949, 315.

³⁰ M. E. Ali and L. N. Owen, *J. Chem. Soc.*, 1958, 2119.

³¹ T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc. (C)*, 1967, 807.

³² L. N. Owen and G. S. Saharia, *J. Chem. Soc.*, 1953, 2582.

of mercury(II) acetate (1.6 g) and the preceding trithiocarbonate (0.41 g) in acetic acid (30 ml) was stirred at 40–45° for 45 min. The mixture was then diluted with chloroform (50 ml), filtered, and concentrated, and the residue was treated with water (50 ml) and extracted with chloroform. The extracts were washed with aqueous sodium hydrogen carbonate and with water, then dried and evaporated to give the *dithiolcarbonate* (0.37 g), m.p. 33–34° (from petroleum) (Found: C, 51.2; H, 6.5; S, 34.3. $C_8H_{12}OS_2$ requires C, 51.0; H, 6.4; S, 34.05%).

trans-1,2-Carbonyldithiocyclopentane (23).—Similar treatment of *trans*-1,2-thiocarbonyldithiocyclopentane¹⁰ (0.18 g) with mercury(II) acetate (0.8 g) in acetic acid (15 ml) gave the *dithiolcarbonate* (0.11 g), m.p. 93–94° (from ether-petroleum) (Found: C, 44.85; H, 5.3; S, 40.2. $C_6H_8OS_2$ requires C, 45.0; H, 5.0; S, 40.0%).

2 β ,3 α -Carbonyldithio-*trans*-decalin (27).—Under the same conditions, 2 β ,3 α -thiocarbonyldithio-*trans*-decalin¹ (0.37 g), with mercury(II) acetate (1.2 g) in acetic acid (25 ml) gave the *dithiolcarbonate* (0.34 g), m.p. 83–84° (from petroleum) (Found: C, 57.7; H, 6.9; S, 27.85. $C_{11}H_{18}OS_2$ requires C, 57.85; H, 7.1; S, 28.1%).

Reagent A.—When the reaction of sodium (wt. specified) with ethanol (vol. specified) was complete, carbon disulphide (at least 30% excess, based on sodium) was slowly added.

Reactions of Cyclic Carbonates and Thiocarbonates with Xanthates.—General Procedure. All reactions were carried out at reflux temperature for the time indicated. The cooled mixture was then diluted with water and extracted with chloroform. The extracts were washed with water, and were then dried and evaporated. Unless otherwise stated, the residue was purified by t.l.c.

(i) A mixture of ethylene carbonate (2.0 g), potassium hydroxide (4.8 g), carbon disulphide (20 ml), and methanol (20 ml) was boiled under reflux for 100 h to give ethylene trithiocarbonate (2.35 g, 22%), m.p. 36–37° (from ether-petroleum) (lit.,³³ 39°). Repetition, with ethanol, propanol, or butanol in place of methanol, gave yields of 25, 50, and 25%, respectively.

(ii) Similar treatment of propylene carbonate (10 g) with potassium hydroxide (56 g), carbon disulphide (80 g), and ethanol (200 ml) gave propylene trithiocarbonate (2.7 g), b.p. 97° at 0.2 mmHg (lit.,³⁴ 136° at 0.2 mmHg).

(iii) *meso*-2,3-Carbonyldioxybutane²⁶ (2.3 g) with Reagent A [from sodium (4.6 g) and ethanol (100 ml)] under reflux for 100 h gave (t.l.c. in ether) DL-2,3-thiocarbonyldithiobutane (0.6 g), m.p. 40–42° (from ether-petroleum) (lit.,¹⁰ 40–41°), τ 5.87 (2H, m) and 8.39 (6H, d).

(iv) DL-2,3-Carbonyldioxybutane²⁶ (2.3 g), treated similarly, gave *meso*-2,3-thiocarbonyldithiobutane (1.1 g), m.p. 39–41° (from ether-petroleum) (lit.,¹² 37–39.5°), τ 5.50 (2H, m) and 8.48 (6H, d).

(v) *meso*-2,3-Thiocarbonyldioxybutane (0.66 g) with Reagent A [from sodium (1.15 g) and ethanol (30 ml)] under reflux for 70 h gave (t.l.c. in chloroform) DL-2,3-thiocarbonyldithiobutane (0.63 g), m.p. 39–41°.

(vi) DL-2,3-Thiocarbonyldioxybutane (1.32 g) with Reagent A [from sodium (2.32 g) and ethanol (50 ml)] similarly gave *meso*-2,3-thiocarbonyldithiobutane (1.20 g), m.p. 38–40.5°.

(vii) *meso*-2,3-Carbonyldithiobutane¹² (0.71 g) with Re-

agent A [from sodium (1.15 g) and ethanol (65 ml)] under reflux for 60 h gave *meso*-2,3-thiocarbonyldithiobutane (0.73 g), m.p. and mixed m.p. 38–40°.

(viii) DL-2,3-Carbonyldithiobutane¹² (1.13 g) with Reagent A [from sodium (1.75 g) and ethanol (125 ml)] under reflux for 24 h gave DL-2,3-thiocarbonyldithiobutane (1.29 g), m.p. and mixed m.p. 38.5–41°.

(ix) A solution of 2,3-carbonyldioxy-2-methylbutane³⁵ (2.0 g) and potassium ethyl xanthate (17.5 g) in ethanol (50 ml) was boiled under reflux for 70 h to give (t.l.c. in ether-chloroform, 1 : 1) 2-methyl-2,3-thiocarbonyldithiobutane (0.33 g), m.p. 64° (from petroleum) (Found: C, 40.2; H, 5.5; S, 54.1. $C_6H_{10}S_3$ requires C, 40.4; H, 5.65; S, 53.9%).

Treatment of this trithiocarbonate (0.26 g) with mercury(II) acetate (1.5 g) in acetic acid (15 ml) for 45 min at 40–45°, as described for the cycloheptane analogue, gave 2,3-carbonyldithio-2-methylbutane (t.l.c. in chloroform-ether, 1 : 1) as an oil (0.11 g) (Found: C, 44.6; H, 6.2; S, 39.5. $C_6H_{10}OS_2$ requires C, 44.4; H, 6.2; S, 39.5%).

(x) 2-Methyl-2,3-thiocarbonyldioxybutane (0.73 g) with Reagent A [from sodium (1.15 g) and ethanol (25 ml)] under reflux for 70 h gave (t.l.c. in chloroform-ether, 1 : 1) 2-methyl-2,3-thiocarbonyldithiobutane (0.14 g), m.p. and mixed m.p. 63–64°.

(xi) *trans*-1,2-Carbonyldithiocyclopentane (80 mg) with Reagent A [from sodium (115 mg) and ethanol (25 ml)] under reflux for 85 h gave (t.l.c. in chloroform-petroleum, 1 : 1) a trace of *trans*-1,2-thiocarbonyldithiocyclopentane, m.p. 146–148° (lit.,¹⁰ 147°).

(xii) *cis*-1,2-Carbonyldioxycyclohexane (0.75 g), potassium hydroxide (2.0 g), carbon disulphide (10 g), and ethanol (25 ml) were boiled together under reflux for 24 h. The product was purified by column chromatography (carbon tetrachloride) to give *trans*-1,2-thiocarbonyldithiocyclohexane (0.29 g), m.p. 169°, identical with an authentic sample.¹

(xiii) *cis*-1,2-Thiocarbonyldioxycyclohexane (0.79 g) with Reagent A [from sodium (1.15 g) and ethanol (30 ml)] under reflux for 100 h, gave the same product (0.57 g), m.p. 169–170°.

(xiv) *trans*-1,2-Carbonyldioxycyclohexane³¹ (1.0 g), potassium hydroxide (2.0 g), carbon disulphide (5 ml), and ethanol (10 ml) were boiled together under reflux for 100 h. Purification as in (xii) gave the same trithiocarbonate (0.17 g), m.p. 169°.

(xv) *trans*-1,2-Thiocarbonyldioxycyclohexane³¹ (0.59 g) with Reagent A [from sodium (0.87 g) and ethanol (30 ml)] under reflux for 100 h, gave (t.l.c. in chloroform) the same product (35 mg), m.p. 169–170°.

(xvi) *trans*-1,2-Carbonyldithiocyclohexane³¹ (0.71 g) with Reagent A [from sodium (0.94 g) and ethanol (25 ml)] under reflux for 100 h, gave the same trithiocarbonate (0.75 g), m.p. 170–171°. Most of the product was precipitated during the initial dilution with water; the remainder was obtained from the residue by t.l.c. (ether).

(xvii) *trans*-1,2-Carbonyldithiocycloheptane (79 mg) with Reagent A [from sodium (0.10 g) and ethanol (25 ml)] under reflux for 75 h, gave (t.l.c. in chloroform-petroleum, 1 : 2), *trans*-1,2-thiocarbonyldithiocycloheptane (79 mg), m.p. and mixed m.p. 66–67°.

(xviii) 2 α ,3 α -Carbonyldioxy-*trans*-decalin (0.39 g) with Reagent A [from sodium (0.46 g) and ethanol (40 ml)] under reflux for 24 h, gave *trans*-decalin-2 α ,3 α -diol (0.21 g),

³³ P. Frassetti, *Ber.*, 1905, **38**, 488.

³⁴ C. C. J. Culvenor and W. Davies, *Austral. J. Sci. Res.*, 1948, **A1**, 236.

³⁵ S. Sarel, L. A. Pohoryles, and R. Ben-Shoshan, *J. Org. Chem.*, 1959, **24**, 1873.

m.p. and mixed m.p. 142—143°. The crude product was colourless (absence of trithiocarbonate).

(xix) 2 α ,3 α -Thiocarbonyldioxy-*trans*-decalin (76 mg) with Reagent A [from sodium (83 mg) and ethanol (16 ml)] under reflux for 18 h, gave (t.l.c. in chloroform) bright yellow crystals (4 mg), m.p. 128—135° (from ether-petroleum), mixed m.p. with 2 β ,3 α -thiocarbonyldithio-*trans*-decalin¹ (m.p. 126—127°) 121—133° (the i.r. spectra were identical).

(xx) 2 β ,3 α -Carbonyldithio-*trans*-decalin (0.46 g) with Reagent A [from sodium (0.46 g) and ethanol (60 ml)] under reflux for 17 h, gave (t.l.c. in chloroform-petroleum, 1:2) bright yellow crystals (0.25 g), m.p. 135—143° (from petroleum), mixed m.p. with the trithiocarbonate (m.p. 126—127°) 127—138° (the i.r. spectra were identical).

(xxi) Methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl- α -D-glucoside (1)³⁶ (0.23 g) with Reagent A [from sodium (0.17 g) and ethanol (50 ml)] under reflux for 24 h, gave (t.l.c. in chloroform) methyl 4,6-*O*-benzylidene- α -D-glucoside (0.17 g), m.p. 171—172°, identical with an authentic specimen (lit.,³⁷ 166—167°).

(xxii) A solution of triethylamine (10 ml) in benzene (60 ml) was added to a stirred mixture of methyl 4,6-*O*-benzylidene- α -D-galactoside³⁸ (2.0 g), ethyl chloroformate (20 ml), and 1,4-dioxan (10 ml) at 0°. After being kept at 5—10° for 2 h, the mixture was washed with 2N-hydrochloric acid and with water, and was then dried and evaporated to a solid residue (1.9 g) which on crystallisation from chloroform-ether afforded methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl- α -D-galactoside, m.p. 224—227°, ν_{\max} 1820 and 1800 cm⁻¹, *m/e* 308 (*M*⁺, 33%), 307 (28), 265 (36), 159 (29), 149 (12), 107 (53), 105 (44), 91 (40), 77 (30), 45 (100), and 43 (12) (Found: C, 58.2; H, 5.5. C₁₅H₁₆O₇ requires C, 58.4; H, 5.2%).

This carbonate (0.62 g) with Reagent A [from sodium (0.46 g) and ethanol (125 ml)] under reflux for 140 h, gave (t.l.c. in chloroform-ether) methyl 4,6-*O*-benzylidene- α -D-galactoside, m.p. and mixed m.p. 171—172°.

(xxiii) A mixture of 1,3-carbonyldioxypropane³⁹ (5 g) and potassium ethyl xanthate (50 g) in ethanol (150 ml) was stirred and boiled under reflux for 90 h. Purification of the product by column chromatography (ether) gave a few mg of yellow crystals. Recrystallisation from ether-

petroleum afforded 1,3-thiocarbonyldithiopropene, m.p. 78—79° (lit.,⁴⁰ 80°). An identical product was obtained in very low yield by treatment of thiacyclobutane⁴¹ (2 g) with potassium ethyl xanthate (21 g) in boiling ethanol (50 ml) for 90 h.

(xxiv) 1,3-Carbonyldioxybutane⁴² (11.6 g) with Reagent A [from sodium (11.5 g) and ethanol (125 ml)] under reflux for 70 h, gave a product from which the yellow component was first separated by column chromatography (ether-chloroform, 1:1) and then purified by t.l.c. (ether-chloroform, 1:1) to afford 1,3-thiocarbonyldithiobutane (0.11 g), m.p. 50.5° (from petroleum), τ 6.3—7.0 (3H, m), 7.15—8.15 (2H, m), and 8.58 (3H, d) (Found: C, 36.5; H, 5.0; S, 58.6. C₅H₈S₃ requires C, 36.5; H, 4.9; S, 58.5%).

Treatment of this trithiocarbonate (100 mg) with mercury(II) acetate (0.5 g) in acetic acid (5 ml) for 45 min at 45°, as described for the cycloheptane compound, gave 1,3-carbonyldithiobutane (40 mg), an oil (purified by t.l.c. in ether) (Found: C, 40.8; H, 5.3; S, 43.2. C₅H₈OS₂ requires C, 40.5; H, 5.4; S, 43.25%).

Reaction of trans-1,2-Carbonyldithiocyclohexane with Sodium NN-Diethyldithiocarbamate.—A mixture of the dithiolcarbonate (0.21 g) and sodium diethyldithiocarbamate trihydrate (1.05 g) in ethanol (25 ml) and water (5 ml) was boiled under reflux for 48 h, then diluted with water and extracted with chloroform. Evaporation of the washed and dried extracts, and purification of the residue by t.l.c. (chloroform) gave *trans*-1,2-thiocarbonyldithiocyclohexane (0.35 g), m.p. 168—170°, identical (i.r. spectrum) with an authentic sample.

Attempted Isomerisation of Thioncarbonates.—(i) A mixture of *cis*-1,2-thiocarbonyldioxy-cyclohexane (0.20 g) and potassium iodide (0.75 g) in acetonitrile (10 ml) was stirred at 70° for 90 h and at reflux temperature for a further 90 h. The residue obtained after evaporation of the solvent was taken up in benzene and washed with water. Evaporation of the dried benzene solution gave starting material (0.19 g) (i.r. spectrum).

(ii) A mixture of *trans*-1,2-thiocarbonyldioxy-cyclohexane (0.10 g) and potassium iodide (0.4 g) in acetonitrile (5 ml) was heated in a sealed tube at 140° for 120 h. The product, isolated as described for the *cis*-isomer, was starting material (0.09 g) (i.r. spectrum).

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³⁶ W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohydrate Res.*, 1967, **4**, 445.

³⁷ J. W. Van Cleve, *Carbohydrate Res.*, 1971, **17**, 461.

³⁸ G. J. Robertson and R. A. Lamb, *J. Chem. Soc.*, 1934, 1321.

³⁹ W. H. Carothers and F. J. Van Natta, *J. Amer. Chem. Soc.*, 1930, **52**, 314.

⁴⁰ W. H. Mills and B. C. Saunders, *J. Chem. Soc.*, 1931, 537.

⁴¹ G. M. Bennett and A. L. Hock, *J. Chem. Soc.*, 1927, 2496.

⁴² S. Searles, D. G. Hummel, S. Nukina, and P. E. Throckmorton, *J. Amer. Chem. Soc.*, 1960, **82**, 2928.