573. *Dithiols. Part IX. Syntheses with the* iso*Propylidene and Benzylidene Derivatives of 2 : 3-Dimercaptopropanol.*

By L. W. C. MILES and L. N. OWEN.

2 : 3 : 4 : 6-Tetra-acetyl β-(2 : 3-*iso*propylidenedithiopropyl)glucoside has been synthesised by reaction of 2 : 3-*iso*propylidenedithiopropanol with acetobromoglucose. Reduction of 2 : 3-*iso*propylidenedithiopropanol with sodium and ethanol in liquid ammonia results in the fission of only one C–S bond, to give (probably) 3-mercapto-2-*iso*propylthiopropanol. 2 : 3-Benzylidenedithiopropyl bromide has been prepared; it is hydrolysed very rapidly in aqueous alkali, and with alkoxides it readily undergoes elimination of hydrogen bromide to give 2 : 3-benzylidenedithiopropene, though it reacts normally with alcohols in the presence of silver oxide to give ethers. Attempts to prepare the toluene-*p*-sulphonyl and methanesulphonyl esters of 2 : 3-*iso*propylidenedithio- and 2 : 3-benzylidenedithio-propanol, by the use of the sulphonyl chloride in pyridine, give only the chlorides and pyridinium derivatives. 2 : 3-Benzylidenedithiopropanol has been isolated in two modifications, which are regarded as *cis*- and *trans*-isomers.

THE ready availability of 2 : 3-dimercaptopropanol (BAL) makes it an attractive potential starting material for the synthesis of other dithiols, but with the exception of certain acylation reactions, which can be carried out so as to affect only the hydroxyl group (Pavlic, Lazier, and Signaigo, *J. Org. Chem.*, 1949, **14**, 59), the high reactivity of the thiol groups necessitates their protection if it is desired to prepare *O*-derivatives.

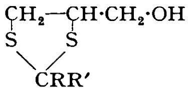
Stocken (*J.*, 1947, 592) described the preparation of the ethylidene, benzylidene, *iso*propylidene, and *cyclo*hexylidene compounds (I), which were all low-melting solids, very stable to hydrolysis; hydrogenolysis of the benzylidene derivative, however, could be accomplished with sodium and ethanol in liquid ammonia, BAL thereby being regenerated.

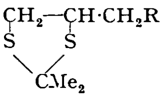
2 : 3-*iso*Propylidenedithiopropanol (II) was first chosen for the present investigation. It reacted very slowly with acetobromoglucose in benzene solution when stirred with silver carbonate. Short-path distillation of the syrup thus obtained gave 2 : 3 : 4 : 6-tetra-acetyl β-(2 : 3-*iso*propylidenedithiopropyl)glucoside (III) as a glass, from which a small amount of crystalline material was obtained; the product from such a reaction is likely to be a mixture of stereoisomers, since, in addition to the possible formation of some α- as well as the β-glucoside, the presence of an asymmetric centre at $C_{(2)}$ in the *n*-propyl group introduces further complications. When the same reaction was carried out with silver oxide in the place of the carbonate, a mixture of (III) and 2 : 3-*iso*propylidenedithiopropyl acetate (IV) was obtained; this provides an interesting example of alcoholysis. The sodium derivative of 2 : 3-*iso*propylidenedithio-

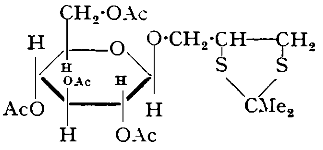
propanol, prepared by the use of naphthylsodium (Scott, Walker, and Hansley, *J. Amer. Chem. Soc.*, 1936, **58**, 2442; Stevens and Deans, *Canadian J. Res.*, 1939, **17**, *B*, 290), gave with acetobromoglucose only (IV), acetolysis now being predominant.

At this stage, it was found that BAL was not regenerated from 2 : 3-*iso*propylidenedithiopropanol by reduction with sodium and ethanol in liquid ammonia, only one of the S–C links being broken under these conditions. The product contained one free thiol group, and can be formulated as (V) or (VI), of which the former, 3-mercapto-2-*iso*propylthiopropanol, is the more probable; with acetone and with benzaldehyde, liquid *iso*propylidene and benzylidene derivatives were formed, and it gave a solid bis-α-naphthylurethane, but no definite proof of its structure has been obtained.

The complete reduction of 2 : 3-benzylidenedithiopropanol under the above conditions (Stocken, *loc. cit.*), however, was confirmed, and experiments directed towards the use of this derivative were therefore undertaken. A more reactive compound was obtained by its conversion into 2 : 3-benzylidenedithiopropyl bromide (VII) by reaction with phosphorus tribromide in carbon tetrachloride or ether. The crude product, m. p. 65°, was obtained in very good yield, but repeated recrystallisation raised the melting point to 81°, and a low yield of the final product was obtained. Alkaline hydrolysis in aqueous dioxan was very fast, and similar to that for the first stage of the hydrolysis of mustard gas (Bartlett and Swain, *J. Amer. Chem. Soc.*, 1949, **71**, 1406); the product was found to be pure 2 : 3-benzylidenedithiopropanol (VIII) which, however, had m. p. 90°, whereas Stocken (*loc. cit.*) recorded m. p. 77° for the compound obtained by the condensation of 2 : 3-dimercaptopropanol with benzaldehyde. Re-investigation of the latter reaction showed that it gave a mixture of isomers, m. p. (after one recrystallisation from benzene–light petroleum) 68—71°, from which the less soluble form, m. p. 88—89°, was isolated by chromatography on alumina and repeated recrystallisation. This isomer is not identical with the material, m. p. 90°, obtained from the bromide, and the two forms are presumably the geometrical isomerides (VIIIa) and (VIIIb). The only previous record of the isolation of a cyclic acetal in two stereoisomeric modifications is apparently of 1 : 3-benzylideneglycerol (Verkade and van Roon, *Rec. Trav. chim.*, 1942, **61**, 831; cf. Davies, Heilbron, and Jones, *J.*, 1934, 1232).

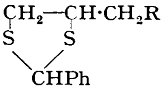

(I.)

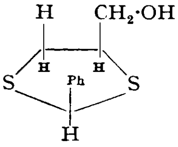

(II; R = OH.)
(IV; R = OAc.)
(XII; R = Cl.)

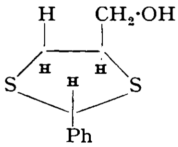

(III.)

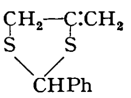
$CH_2(SH)\cdot CH(SPr^i)\cdot CH_2\cdot OH$
(V.)

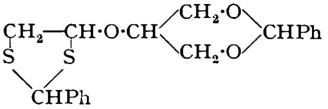
$CH_2(SPr^i)\cdot CH(SH)\cdot CH_2\cdot OH$
(VI.)

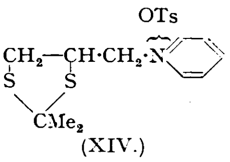

(VII; R = Br.)
(VIII; R = OH.)
(X; R = OMe.)
(XIII; R = Cl.)

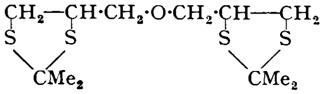

(VIIIa.)

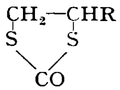

(VIIIb.)

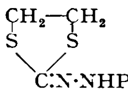

(IX.)


(XI.)


(XIV.)


(XV.)


(XVI; R = CH₂·OH.)
(XVII; R = H.)


(XVIII.)

2 : 3-Benzylidenedithiopropyl bromide reacted readily with sodium methoxide in methanol and gave a mixture, from which 2 : 3-benzylidenedithiopropene (IX) was separated, showing

that some intramolecular loss of hydrogen bromide had occurred. The same compound was obtained by reaction of the bromide with the sodium derivative of 1 : 3-dimethoxypropan-2-ol in excess of the alcohol or in benzene, in which the sodium salt was surprisingly soluble. In each case the methylenic product was formed at room temperature, and in high yield; originally obtained as a mobile liquid, it crystallised after redistillation and was stable at 0°, but it quickly liquefied and darkened when left at room temperature. The structure assigned is in accordance with the light absorption (max. 2280, 2360 A.; $\varepsilon = 10,000$) and with the results of ozonolysis which gave benzaldehyde, hydrogen sulphide, and a small quantity of formaldehyde. Treatment of (IX) with mercuric chloride in methanol brought about ring-fission and precipitated a mercurichloride complex, but decomposition of the latter with hydrogen sulphide gave no recognisable product. Analogous oxygen compounds, of proved structure, have been obtained by heating cyclic acetals of glycerol α-chlorohydrin with potassium hydroxide (Fischer, Baer, and Feldmann, *Ber.*, 1930, **63**, 1732; cf. Davies and Oxford, *J.*, 1931, 224).

Under milder conditions, namely, stirring with silver oxide in dry methanol, 2 : 3-benzylidenedithiopropyl bromide gave 2 : 3-benzylidenedithiopropyl methyl ether (X); similarly, with silver oxide and 1 : 3-benzylideneglycerol in benzene, a liquid was obtained which was probably 1 : 3-benzylidenedioxyprop-2-yl 2 : 3-benzylidenedithiopropyl ether (XI) since it appeared to be identical with the product formed by the condensation of benzaldehyde and 1 : 3-dihydroxyprop-2-yl 2 : 3-dimercaptopropyl ether (Evans and Owen, *J.*, 1949, 244). The bromide also reacted normally with potassium thiolacetate in ethanol, to give 2 : 3-benzylidenedithiopropyl thiolacetate (see Part X, following paper).

Attention was also directed to the preparation of toluene-*p*-sulphonyl and methanesulphonyl esters of 2 : 3-*iso*propylidenedithio- and 2 : 3-benzylidenedithio-propanol, since such derivatives might provide other routes to the ethers. Under the standard conditions (cf. Tipson, *J. Org. Chem.*, 1944, **9**, 235), treatment with toluene-*p*-sulphonyl or methanesulphonyl chloride in cold pyridine gave no sulphonyl esters, but the corresponding chlorides (XII) and (XIII) were obtained in good yield; no significant amount of pyridine hydrochloride separated at any stage in the reaction. From the water-soluble fraction of the product from the reaction of 2 : 3-*iso*propylidenedithiopropanol and toluene-*p*-sulphonyl chloride, a small quantity of 2 : 3-*iso*propylidenedithiopropylpyridinium toluene-*p*-sulphonate (XIV) was obtained. Tipson (*loc. cit.*) has pointed out that chlorides and pyridinium compounds are both formed from toluene-*p*-sulphonates, and may result if the conditions of the toluene-*p*-sulphonation are not sufficiently mild. In the present instance, it appears that the desired sulphonyl esters are so reactive that the secondary transformations occur extremely readily; this, perhaps, is not surprising in view of the high reactivity of the bromide (VII) and of other substituted sulphides (cf. Baddeley, *J.*, 1950, 663). The appearance of only a small amount of pyridine hydrochloride during the reactions also indicates that the sulphonyl esters have only a transitory existence. Attempts to obtain them by other methods (*e.g.*, that of Hahn and Walter, *Ber.*, 1921, **54**, 1531) proved equally unsuccessful. The reaction of 2 : 3-*iso*propylidenedithiopropanol with toluene-*p*-sulphonyl chloride in an aqueous acetone solution of sodium hydroxide gave only di-(2 : 3-*iso*propylidenedithiopropyl) ether (XV); this again is a secondary product, probably formed *via* the toluene-*p*-sulphonate.

In view of the resistance towards hydrolysis shown by the cyclic acetals of 2 : 3-dimercaptopropanol, the synthesis of the corresponding cyclic dithiolcarbonate (XVI) was considered, in the hope that regeneration from such a derivative would be more readily achieved. However, treatment of 2 : 3-dimercaptopropanol with ethyl chloroformate and with carbonyl chloride (cf. Haworth *et al.*, *J.*, 1924, **125**, 1223; 1926, 1751; 1929, 2796) gave complex polymeric products. Busch and Lingenbrink (*J. pr. Chem.*, 1854, **61**, 337) recorded the formation of the cyclic dithiolcarbonate (XVII) by hydrolysis of the phenylhydrazone (XVIII), which they prepared from ethylene dibromide and the phenylhydrazone of potassium dithiolcarbonate. Using the more accessible ammonium dithiolcarbonate (Heller and Bauer, *ibid.*, 1855, **65**, 382), however, we failed to effect a similar reaction with 2 : 3-dibromopropanol in ethanol at 100°, the only result being the hydrolysis and rearrangement of the dithiolcarbonate, 1-phenyl- and 1 : 4-diphenyl-thiosemicarbazide being obtained.

EXPERIMENTAL.

2 : 3 : 4 : 6-*Tetra-acetyl β-(2 : 3-*iso*Propylidenedithiopropyl)glucoside*.—(i) α-D-Acetobromoglucose (11·5 g.) and 2 : 3-*iso*propylidenedithiopropanol (6 g., 15% excess) were dissolved in dry benzene (150 c.c.); silver carbonate (9 g.), anhydrous calcium sulphate (10 g.), and iodine (2 g.) were added. The suspension was stirred for 4 days, and the reaction was completed by boiling under reflux for 24 hours. The filtered solution was washed with aqueous sodium thiosulphate, then with water, and dried ($CaCl_2$). Evaporation

gave a syrup, from which crystals of 2 : 3-*iso*propylidenedithiopropanol separated. Short-path distillation separated further excess of this compound, b. p. 75° (bath)/0·0001 mm., from the required 2 : 3 : 4 : 6-*tetra-acetyl* β-(2 : 3-iso*propylidenedithiopropyl)glucoside* (7·9 g.), b. p. 170—180° (bath)/0·0001 mm., which was obtained as a pale straw-coloured glass (Found : C, 48·3; H, 6·2; Ac, 40·8. $C_{20}H_{30}O_{10}S_2$ requires C, 48·6; H, 6·1; Ac, 41·6%). Careful addition of water to a solution of a portion of the glass in acetic acid, and storage at 0° for several weeks, resulted in partial crystallisation. Recrystallisation from light petroleum, then from ethyl acetate, gave one *isomer*, m. p. 122° (corr.) (Found : S, 13·0. $C_{20}H_{30}O_{10}S_2$ requires S, 13·0%).

(ii) α-D-Acetobromoglucose (7·5 g.) and 2 : 3-*iso*propylidenedithiopropanol (10 g.) were dissolved in dry benzene (50 c.c.), silver oxide (10 g.) and anhydrous calcium sulphate (10 g.) were added, and the suspension was shaken in a stoppered bottle for 5 weeks. Filtration, evaporation, and distillation gave 2 : 3-iso*propylidenedithiopropyl acetate* (3·6 g.), b. p. 65°/0·01 mm., n_D^{19} 1·5190 (Found : C, 46·5; H, 7·0. $C_8H_{14}O_2S_2$ requires C, 46·6; H, 6·8%), and the required higher-boiling tetra-acetate (4·5 g.), again as a glass. Catalytic deacetylation of the former, by treatment in methanol with a trace of sodium, gave 2 : 3-*iso*propylidenedithiopropanol, m. p. and mixed m. p. 52°.

(iii) Sodium (2 g.) was added in small pieces to a solution of naphthalene (4 g.) in the cyclic formal of ethylene glycol (nordioxan) (20 c.c.). After being stirred for 2½ hours, titration of a portion of the solution with sulphuric acid showed that 1·8 g. of sodium had reacted. The excess of sodium was removed, and the dark red solution was cooled in a carbon dioxide–ethanol bath. The addition of a solution of 2 : 3-*iso*propylidenedithiopropanol (5 g.) in nordioxan (5 c.c.) gave a pale-yellow solution, which gave no reaction for free thiol with aqueous sodium nitroprusside. α-D-Acetobromoglucose (12 g.) in the same solvent (25 c.c.) was then added dropwise, a gelatinous precipitate being formed immediately. The solution was allowed to warm to room temperature, and was set aside for 24 hours. It was then diluted with water (150 c.c.) and extracted with chloroform. Titration of a portion of the neutralised aqueous solution with silver nitrate showed that 80% of the bromine had been converted into bromide ion. The chloroform extract was dried (Na_2SO_4) and evaporated, and distillation of the residue gave 2 : 3-*iso*propylidenedithiopropyl acetate (6·3 g.), b. p. 60°/0·001 mm., n_D^{15} 1·5250.

3-*Mercapto*-2-iso*propylthiopropanol*.—To a solution of 2 : 3-*iso*propylidenedithiopropanol (10 g.) in liquid ammonia (200 c.c.), ethanol (1 c.c.) and small pieces of sodium (10 g.) were added, with stirring. A dark-blue solution was thus obtained, and after 1 hour the excess of sodium was decomposed by the addition of solid ammonium chloride, and the ammonia was allowed to evaporate. The residue was dissolved in water, and acidified with hydrochloric acid. Extraction with ether and evaporation of the dried (Na_2SO_4) extract gave a pale yellow oil (8·5 g.) (Found : thiol-S, 18·0%). Distillation gave (probably) 3-*mercapto*-2-iso*propylthiopropanol* (7·6 g., 75%), b. p. 75°/0·5 mm., n_D^{20} 1·5286 (Found : C, 43·1; H, 8·5; thiol-S, 19·3. $C_6H_{14}OS_2$ requires C, 43·3; H, 8·5; thiol-S, 19·3%).

The hydroxy-thiol (1·75 g.) was dissolved in benzene, benzaldehyde (1·25 g.) was added, and hydrogen chloride was passed in for 1 minute. An exothermic reaction took place, and water was formed. Washing with aqueous potassium carbonate, then with water, removal of the benzene, and distillation of the residue gave the *benzylidene* derivative (2·1 g.), b. p. 125°/0·5 mm., n_D^{20} 1·5765 (Found : C, 61·4; H, 7·2; S, 25·3. $C_{13}H_{18}OS_2$ requires C, 61·4; H, 7·1; S, 25·2%). Similarly, the iso*propylidene* derivative, b. p. 80°/1 mm., n_D^{23} 1·5134, was obtained (Found : C, 52·3; H, 9·0. $C_9H_{18}OS_2$ requires C, 52·4; H, 8·8%).

A solution of the hydroxy-thiol (0·3 g.) and α-naphthyl *iso*cyanate (0·6 g.) in light petroleum containing a trace of diethylaniline was kept at 80° for 2 hours. The *bis-α-naphthylurethane* (0·7 g.) was thus obtained, m. p. 145°, after recrystallisation from chloroform–light petroleum (Found : C, 66·4; H, 5·7. $C_{28}H_{28}O_3N_2S_2$ requires C, 66·6; H, 5·6%).

2 : 3-*Benzylidenedithiopropyl Bromide*.—2 : 3-Benzylidenedithiopropanol (20 g.) was suspended in dry ether (100 c.c.), and phosphorus tribromide (10 g.) was added dropwise during 1 hour, the temperature being kept below 0°. After 12 hours at room temperature, the clear ethereal solution was decanted from the lower layer of phosphorus acids and was washed with aqueous sodium hydrogen carbonate. Evaporation of the dried (Na_2SO_4) solution and recrystallisation of the residue from hot ethanol gave 2 : 3-*benzylidenedithiopropyl bromide* (mixed isomers), m. p. 65° (22 g., 85%). Repeated recrystallisation from ethanol–ether raised the m. p. to 81° (Found : C, 43·8; H, 4·2; S, 23·3; Br, 29·5. $C_{10}H_{11}S_2Br$ requires C, 43·6; H, 4·0; S, 23·3; Br, 29·0%).

cis- *and* trans-*Isomers of* 2 : 3-*Benzylidenedithiopropanol*.—2 : 3-Benzylidenedithiopropyl bromide, m. p. 81° (0·662 g.), was accurately weighed into a 500-c.c. graduated flask and dissolved in dioxan (200 c.c.) freshly distilled from sodium. 0·1N-Sodium hydroxide (200 c.c.) was added, and the solution was quickly made up to the mark with dioxan and well mixed. After 10 minutes at 20°, 100 c.c. were removed and titrated against 0·1073N-hydrochloric acid, using screened methyl-red indicator, a blank determination, without the bromide, being done in the same way. The alkali consumed was equivalent to 4·60 c.c. of the acid. After 20 minutes, the determination was repeated, with identical results, which correspond to complete hydrolysis, with a rate constant of at least 0·5, assuming the reaction to be of the first order.

Dilution of the acidified solution and extraction with chloroform (25 c.c.) gave a solid (0·3 g.), m. p. 88°. One recrystallisation from benzene raised the m. p. to a constant value of 90°. The hydrolysis was repeated in more concentrated solution (0·6 g. in 15 c.c. of dioxan and 10 c.c. of 2N-sodium hydroxide), and the same product (0·25 g.) was obtained. Recrystallisation from benzene–light petroleum gave clusters of small plates, m. p. 90°, of one isomer of 2 : 3-*benzylidenedithiopropanol* (Found : C, 56·65; H, 5·7; S, 29·9%; *M*, 113. $C_{10}H_{12}OS_2$ requires C, 56·6; H, 5·7; S, 30·2%; *M*, 112·2).

The condensation of 2 : 3-dimercaptopropanol and benzaldehyde in benzene, and one recrystallisation of the product from benzene–light petroleum (b. p. 60—80°) gave a product of m. p. 68—71°. Chromatography of this material (0·5 g.) on alumina, with benzene as eluent, gave 0·2 g. of a more firmly-held fraction, m. p. 72—78° (after one recrystallisation). Re-chromatography of this gave a fraction (70 mg.), m. p. 75—81°. Recrystallisation (5 times) then raised the m. p. to a constant value of 88—89°. This pure isomeric 2 : 3-*benzylidenedithiopropanol* crystallised in clusters of flat needles (Found : C, 56·7; H, 5·8; S, 30·25. $C_{10}H_{12}OS_2$ requires C, 56·6; H, 5·7; S, 30·2%). The mixed m. p. of the two isomers was 69—72°.

2 : 3-*Benzylidenedithiopropene*.—(i) A solution of 2 : 3-benzylidenedithiopropyl bromide (6 g.) and sodium (1 g.) in dry methanol (10 c.c.) was heated under reflux for 3 hours. The cooled solution was made neutral to Congo-red with hydrochloric acid, diluted with water, and extracted with ether. The extract was dried ($CaCl_2$) and the ether was removed by distillation. The residual liquid (4·4 g.) on distillation appeared to consist of a mixture of two compounds of closely similar boiling points. Careful fractionation separated some of the lower-boiling constituent, 2 : 3-*benzylidenedithiopropene*, b. p. 90°/0·01 mm., n_D^{20} 1·6348, which was probably the major product (Found : S, 32·6. $C_{10}H_{10}S_2$ requires S, 33·0%). Light absorption : max. 2280, 2360 A., ε = 10,000 and 10,000. The colourless mobile liquid soon became dark red and viscous.

(ii) 1 : 3-Dimethoxypropan-2-ol (2·6 g.) was dissolved in liquid ammonia (50 c.c.), and sodium (0·5 g.) was added in small pieces. After 30 minutes, a clear colourless solution was obtained, and the ammonia was allowed to evaporate. The white solid thus obtained was dissolved in dry benzene (20 c.c.) and a solution of 2 : 3-benzylidenedithiopropyl bromide (5·5 g.) in benzene (15 c.c.) was added. A precipitate was soon formed, and after 2 days at room temperature the sodium bromide (2·1 g., 95%) was collected by filtration. Removal of the benzene and short-path distillation at 90° (bath)/0·0001 mm. gave unchanged 1 : 3-dimethoxypropan-2-ol (2·2 g., 85%), collected in the liquid-air trap and subsequently re-distilled (b. p. 167°/768 mm., n_D^{22} 1·4230), and 2 : 3-benzylidenedithiopropene (2·1 g., 54%), which crystallised spontaneously, and formed white needles, m. p. 52°, when recrystallised from light petroleum (b. p. 40—60° (Found : C, 62·3; H, 5·2. Calc. for $C_{10}H_{10}S_2$: C, 61·8; H, 5·1%). It showed the same light absorption as the liquid described above (max. : 2280, 2360 A.; ε = 10,000 and 10,000 in ethanol; 11,000 and 13,000 in hexane). A polymeric residue was left in the retort.

Ozonisation. A slow stream of ozonised oxygen was passed through a solution of 2 : 3-benzylidenedithiopropene (1 g.) in ethyl acetate (5 c.c.), cooled in ice, for 1·5 hours, the exit gases being passed through water; the presence of formaldehyde in these washings was shown by formation of the dimedone derivative (40 mg.), m. p. 189°. The ethyl acetate solution was concentrated and the residue was decomposed with zinc dust and water, hydrogen sulphide being evolved. Steam-distillation, ether-extraction of the distillate, and addition of the product to 2 : 4-dinitrophenylhydrazine sulphate in methanol gave benzaldehyde 2 : 4-dinitrophenylhydrazone (0·65 g.), m. p. and mixed m. p. 140°.

2 : 3-*Benzylidenedithiopropyl Methyl Ether*.—2 : 3-Benzylidenedithiopropyl bromide (5 g.) was dissolved in dry methanol (40 c.c.), and silver oxide (5 g.) was added. After 4 days at room temperature, with occasional stirring, the silver salts were removed by filtration, and the filtrate was concentrated. Distillation of the residue gave 2 : 3-*benzylidenedithiopropyl methyl ether* (1·8 g.), a colourless liquid, b. p. 100°/0·0001 mm., n_D^{20} 1·5990 (Found : S, 28·2. $C_{11}H_{14}OS_2$ requires S, 28·3%).

1 : 3-*Benzylidenedioxyprop-2-yl 2* : 3-*Benzylidenedithiopropyl Ether*.—(i) 1 : 3-Dihydroxyprop-2-yl 2 : 3-dimercaptopropyl ether (0·5 g.) (Evans and Owen, *loc. cit.*) was dissolved in benzene (3 c.c.); benzaldehyde (0·55 g.) was added and hydrogen chloride was passed through for 1 minute. After being washed with water and dried (Na_2SO_4), the benzene solution was concentrated. Distillation of the residue gave 1 : 3-*benzylidenedioxyprop-2-yl 2* : 3-*benzylidenedithiopropyl ether* as a colourless viscous liquid, b. p. 130—140° (bath)/0·0001 mm., n_D^{15} 1·6041 (Found : S, 17·4. $C_{20}H_{22}O_3S_2$ requires S, 17·1%).

(ii) 2 : 3-Benzylidenedithiopropyl bromide (0·2 g.) and 1 : 3-benzylideneglycerol (0·15 g.) were dissolved in dry benzene (8 c.c.), silver oxide (0·5 g.) was added, and the solution was heated under reflux for 12 hours. Filtration and evaporation of the filtrate, followed by micro-distillation at 0·0001 mm., gave a viscous, pale-yellow liquid, n_D^{20} 1·6020.

2 : 3-iso*Propylidenedithiopropyl Chloride*.—Toluene-*p*-sulphonyl chloride (7·4 g.) was added to a solution of 2 : 3-*iso*propylidenedithiopropanol (6 g.) in dry pyridine (30 c.c.) cooled in ice–salt. Only a trace of pyridine salt crystallised out. After 4 hours at 0°, the solution was diluted with ice-water and extracted with chloroform; the product was an oil, distillation of which gave pure 2 : 3-*iso*propylidenedithiopropyl chloride (3·5 g., 52%), b. p. 54°/0·1 mm., n_D^{12} 1·5535 (Found : C, 40·0; H, 6·1. Calc. for $C_6H_{11}S_2Cl$: C, 39·5; H, 6·0%); Stocken (*J.*, 1947, 592) reported b. p. 80°/0·7 mm. When the chloride was boiled with 2N-sodium hydroxide for 2 minutes, 2 : 3-*iso*propylidenedithiopropanol, m. p. and mixed m. p. 52°, was obtained.

Further extraction of the diluted reaction mixture with chloroform gave a crystalline solid (0·15 g.). Recrystallisation from aqueous dioxan (90%) gave plates of 2 : 3-iso*propylidenedithiopropylpyridinium toluene*-p-*sulphonate*, m. p. 135—136°, soluble in water, alcohol, ether, or benzene, but insoluble in light petroleum (Found : C, 53·9; H, 5·6. $C_{18}H_{23}O_3NS_3$ requires C, 54·4; H, 5·8%). The aqueous-dioxan solution gave a white precipitate when aqueous mercuric chloride was added.

2 : 3-*Benzylidenedithiopropyl Chloride*.—Methanesulphonyl chloride (7·5 g.) was added portion-wise, with frequent shaking, to a solution of 2 : 3-benzylidenedithiopropanol, m. p. 71° (10 g.), in dry pyridine (60 c.c.) cooled in ice–salt. After 6 hours, ice-water (60 c.c.) was added in portions, and the precipitated solid (9 g., 84%), m. p. 60°, was collected by filtration. Recrystallisation from ethanol gave 2 : 3-benzylidenedithiopropyl chloride (4 g.), m. p. and mixed m. p. with authentic material (Stocken, *loc. cit.*) 70—71°.

Di-(2 : 3-iso*propylidenedithiopropyl*) *Ether*.—To a solution of 2 : 3-*iso*propylidenedithiopropanol (3 g.) in acetone (25 c.c.), 10% aqueous sodium hydroxide (20 c.c.) was added. The mixture was cooled in an ice–salt bath, and a solution of toluene-*p*-sulphonyl chloride (4 g.) in acetone was added dropwise with vigorous stirring. Stirring was continued overnight, and the solid (1·2 g.) was collected by filtration and washed with water. Recrystallisation from ethanol gave *di-*(2 : 3-iso*propylidenedithiopropyl*) *ether*, m. p. 79° (Found: C, 46·0; H, 7·0. $C_{12}H_{22}OS_4$ requires C, 46·4; H, 7·1%). Dilution with water of the liquid portion of the reaction mixture gave a further quantity (1 g.) of less pure material.

Attempted Preparation of Cyclic Dithiolcarbonates.—(i) A mixture of 2 : 3-dimercaptopropanol (5 g.) and ethyl chloroformate (4·8 g.) was cooled in ice–salt, and 10% aqueous sodium hydroxide (40 c.c.) was run in dropwise with vigorous stirring, in nitrogen. After 2 hours the mixture was extracted with chloroform. The extract was washed with dilute sodium hydroxide solution, then with water, and dried (Na_2SO_4). Removal of the solvent left an evil-smelling oil (1·2 g.), from which no crystalline material could be obtained by reaction with α-naphthyl *iso*cyanate. The oil distilled over the range 74—140°/1 mm., and the distillate was not homogeneous (n_D^{20} 1·5170—1·5390). Acidification of the alkaline solution and further extraction gave polymeric material which gave a positive test for free thiol groups.

(ii) 2 : 3-Dimercaptopropanol (10 g.) was dissolved in pyridine (20 c.c.), and carbon tetrachloride (50 c.c.) was added. The solution was cooled in ice, and carbonyl chloride was passed in with vigorous stirring. After 40 minutes the solution was diluted with ice-water, and excess of sodium hydrogen carbonate was added. The carbon tetrachloride layer was separated and washed with 2N-sodium hydroxide, water, N-hydrochloric acid, and finally with water. The dried (Na_2SO_4) solution was concentrated under reduced pressure, and a dark brown oil (3 g.) obtained, which rapidly decomposed on storage.

(iii) 2 : 3-Dimercaptopropanol (5 g.) was dissolved in dry benzene (50 c.c.), potassium carbonate (10 g.) was added, the solution was cooled in ice-salt, and carbonyl chloride was passed in for 15 minutes. The solution was stirred for 5 hours, and then filtered into 2N-sodium hydroxide solution. The benzene layer was separated and washed successively with dilute alkali, water, acid, and sodium hydrogen carbonate solution. Removal of the solvent from the dried (Na_2SO_4) solution gave a colourless oil (4·5 g.) which decomposed on attempted distillation at 10^{-4} mm.

(iv) 2 : 3-Dibromopropanol (6 g.) and the phenylhydrazone of ammonium dithiolcarbonate (Heller and Bauer, *loc. cit.*) (6 g.) in ethanol (50 c.c.) were heated at 90° for 5 hours. On cooling, ammonium bromide (1 g.) crystallised. Dilution with water and extraction with ether gave an oil (7·5 g.) which was triturated with benzene. The benzene-insoluble fraction (0·3 g.) crystallised from ethanol in plates, and was 1-phenylthiosemicarbazide, m. p. 201° (Found: C, 50·5; H, 5·3; N, 26·3. Calc. for $C_7H_9N_3S$: C, 50·3; H, 5·4; N, 25·2%). From the benzene solution 1 : 4-diphenylthiosemicarbazide (0·5 g.) was obtained, m. p. (corr.) and mixed m. p. with an authentic specimen (Heller and Bauer, *loc. cit.*) 175°.

When the 1-phenylthiosemicarbazide was warmed on the steam-bath for 2 minutes with excess of acetic anhydride it dissolved, and an *acetyl* derivative crystallised from the hot solution, m. p. (corr.) 218° after recrystallisation from ethanol (Found: C, 51·9; H, 5·1. $C_9H_{11}ON_3S$ requires C, 51·7; H, 5·3%). Light absorption: max. 2460 A., $E^{1\%}_{1\,\text{cm.}}$ 1080. This solid was clearly not identical with the compound, m. p. 178—179°, prepared in very low yield by Dixon (*J.*, 1889, **55**, 303) by reaction of phenylhydrazine with acetyl *iso*thiocyanate, and considered by him to be 4-acetyl-1-phenylthiosemicarbazide.

Absorption spectra were kindly determined by Dr. E. A. Braude. We thank the Medical Research Council for a maintenance grant (to L. W. C. M.).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

[*Received, July* 15*th*, 1950.]