**149.** *Dithiols. Part XII.* The Alkaline Hydrolysis of Acetylated Hydroxy-thiols : A New Reaction for the Formation of Cyclic Sulphides.*

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

Deacetylation, with dilute aqueous alkali, of either the *O*- or the *S*-acetyl derivative of 2-mercaptoethanol leads to the formation of ethylene sulphide and polymeric material. *cyclo*Hexene sulphide is obtained in good yield by deacetylation of the *O*- or *S*-acetyl derivative of *trans*-2-mercapto*cyclo*hexanol with hot aqueous sodium carbonate; under more vigorous conditions the sulphide undergoes further reactions. Anomalous results reported earlier in the alkaline deacetylation of triacetyl 2 : 3-dimercaptopropanol (triacetyl BAL) have been fully explained; the initial product is 3-acetylthiopropylene sulphide, which under mild conditions can be isolated (yield 80%), but otherwise reacts further to give 3-hydroxy-2 : 2′ : 3′-trimercaptodipropyl sulphide and more complex products. 3-Acetylthiopropylene sulphide is also formed from the di-*S*-acetyl derivative of 2 : 3-dimercaptopropanol, whilst 2 : 3-dimercaptopropyl acetate gives 3-mercaptopropylene sulphide. The *O*- and di-*S*-acetyl derivatives of 3 : 4-dimercaptobutanol give 3-mercaptothiophan, the ring structure of which is proved by partial desulphurisation to thiophan. Cyclisation does not occur on alkaline deacetylation of the *O*- or the *S*-acetyl derivative of 2-hydroxy-2′-mercaptodiethyl sulphide. The formation of cyclic sulphides occurs through intramolecular elimination of acetic acid, and involves ester fission of the *O*-alkyl type.
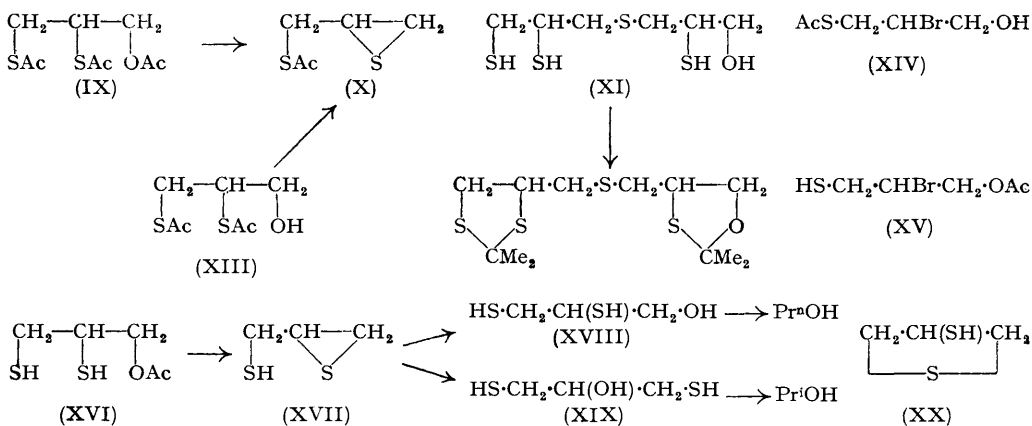
DURING studies carried out in these laboratories on the synthesis and reactions of dithiols, it has been observed that the deacetylation of acetylated hydroxy-thiols frequently proceeds abnormally, in that the thiol value of the hydrolysed material does not attain the theoretical (see, *e.g.*, Evans and Owen, *J.*, 1949, 244). In this connection the observation of Pavlic, Lazier, and Signaigo (*J. Org. Chem.*, 1949, **14**, 59), that 2 : 3-dimercaptopropyl acetate is rapidly hydrolysed in aqueous solution, is of interest, because it indicates that the presence of thiol groups can greatly increase the reactivity of a neighbouring acetyl group. As a first step in the investigation of these possibly related phenomena, it seemed desirable to find to what extent the presence of only one vicinal thiol group produced the same effects.
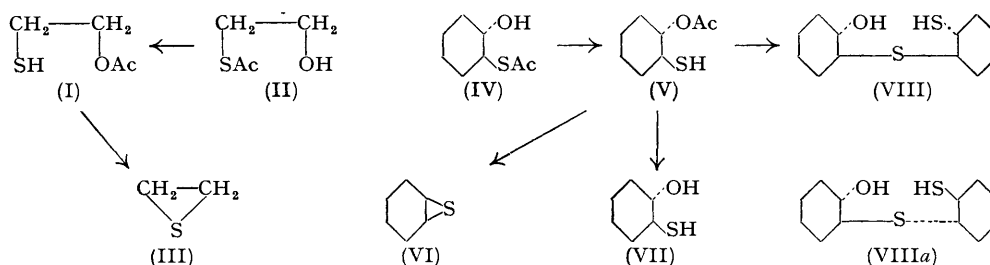
2-Mercaptoethyl acetate (I) has been obtained (Nylen and Olsen, *Svensk Kem. Tidsk.*, 1941, **53**, 274) by rearrangement of the isomeric thiolacetate (II) by heating it in aqueous solution; clearly, therefore, (I) is more stable than 2 : 3-dimercaptopropyl acetate. It has now been prepared by direct acetylation of 2-mercaptoethanol, following the method of Pavlic, Lazier, and Signaigo (*loc. cit.*), and although it was not decomposed in neutral solution it was rapidly hydrolysed in the presence of a small excess of cold dilute alkali to give ethylene sulphide (III) and much polymer. Nylen and Olsen (*loc. cit.*) reported the formation of polymer in the reaction of alkali with the isomer (II), and considered it to have been derived from the free hydroxy-thiol, but this explanation is untenable since 2-mercaptoethanol is stable in alkaline solution. There can be little doubt that the polymer is formed from ethylene sulphide and that the latter is an initial product of the deacetylation.

* Part XI, Owen and Smith, *J.*, 1951, 2973.

The corresponding *cyclo*hexane compounds were chosen for further investigation of the reaction, because of the greater stability and ease of isolation of *cyclo*hexene sulphide (cf. Culvenor, Davies, and Pausacker, *J.*, 1946, 1050). The addition of thiolacetic acid to *cyclo*hexene oxide took place readily at room temperature to give *trans*-2-acetylthio*cyclo*-hexanol (IV) in good yield. This was stable to heat when pure, but at 100° in the presence of 1% of acetic acid it rearranged to the *O*-acetate (V) (cf. Sjöberg, *Ber.*, 1941, **74**, 64), which had earlier been obtained in poor yield by the addition of acetic acid to *cyclo*hexene sulphide (Culvenor, Davies, and Heath, *J.*, 1949, 282). By hydrolysis of the *O*-acetate with sodium hydroxide in aqueous alcohol there were obtained a trace of *cyclo*hexene sulphide (VI), *trans*-2-mercapto*cyclo*hexanol (VII), 2-hydroxy-2'-mercaptodi*cyclo*hexyl sulphide (VIII), and some polymer. However, when either (IV) or (V) was "steam-distilled" with aqueous sodium carbonate at 60° under reduced pressure, *cyclo*hexene sulphide was obtained in 70% yield from the distillate. The primary product of the deacetylation was therefore *cyclo*hexene sulphide, which under the more vigorous conditions of the earlier experiment had undergone ring-fission and had been largely converted into (VII), (VIII), and polymers. It may be observed that (VIII), formed by interaction of (VI) and (VII), although possessing a *trans*-configuration at each *cyclo*hexane ring (on the assumption that the usual Walden inversion occurs when the sulphide ring is opened) can nevertheless exist in two stereoisomeric forms, (VIII) and (VIIIa) (cf. Owen and Smith, *J.*, 1951, 2973). It was obtained as a liquid, but it gave a crystalline 2 : 4-dinitrophenyl derivative which appeared to be homogeneous, and no indication was obtained of the presence of another stereoisomer.

$$CH_2—CH—CH_2 \qquad \rightarrow \qquad CH_2—CH—CH_2 \qquad CH_2·CH·CH_2·S·CH_2·CH·CH_2 \qquad AcS·CH_2·CHBr·CH_2·OH$$

(schematic reaction diagram with structures labelled IX, X, XI, XIV, XIII, XV, and CMe$_2$ ketal structures, and lower row XVI, XVII, XVIII, XIX, XX)

$$\begin{array}{cccc} CH_2—CH—CH_2 & & CH_2·CH·CH_2·S·CH_2·CH·CH_2 & AcS·CH_2·CHBr·CH_2·OH \\ |\quad |\quad | & & |\quad |\qquad\qquad |\quad | & \\ SAc\;\; SAc\;\; OAc & SAc\quad S & SH\;\; SH\qquad\qquad SH\;\; OH & (XIV) \\ (IX) & (X) & (XI) & \end{array}$$

$$\begin{array}{ccc} CH_2—CH—CH_2 & CH_2—CH·CH_2·S·CH_2·CH—CH_2 & HS·CH_2·CHBr·CH_2·OAc \\ |\quad |\quad | & |\quad |\qquad\qquad\quad |\quad | & \\ SAc\;\; SAc\;\; OH & S\quad S\qquad\qquad\quad S\quad O & (XV) \\ (XIII) & CMe_2\qquad\qquad CMe_2 & \end{array}$$

$$\begin{array}{ccc} & HS·CH_2·CH(SH)·CH_2·OH \longrightarrow Pr^nOH & \\ CH_2—CH—CH_2 \;\rightarrow\; CH_2·CH—CH_2\;\nearrow & (XVIII) & CH_2·CH(SH)·CH_2 \\ |\quad |\quad |\qquad\qquad\quad |\quad | & & |\underline{\qquad\quad}S\underline{\qquad\quad}| \\ SH\;\; SH\;\; OAc\qquad\quad SH\quad S\;\;\searrow & HS·CH_2·CH(OH)·CH_2·SH \longrightarrow Pr^iOH & (XX) \\ (XVI)\qquad\qquad (XVII) & (XIX) & \end{array}$$

In the light of the above results, the alkaline hydrolysis of the triacetyl derivative (IX) of 2 : 3-dimercaptopropanol (Evans, Fraser, and Owen, *J.*, 1949, 248) was re-investigated. 2 : 3-Dimercaptopropanol was obtained in 35% yield, and shown to be homogeneous by desulphurisation with Raney nickel, oxidation of the product, and identification of the propaldehyde thus obtained as its 2 : 4-dinitrophenylhydrazone. A higher-boiling fraction of the hydrolysis product is formulated as 3-hydroxy-2 : 2' : 3'-trimercaptodipropyl sulphide (XI), which formed a crystalline di*iso*propylidene derivative (XII). When (IX) was treated with aqueous sodium carbonate under the same conditions as for the *cyclo*-hexane compounds, the probable intermediate in the above reaction, 3-acetylthiopropylene sulphide (X), was obtained in 80% yield; it reacted slowly with methyl iodide to give trimethylsulphonium iodide, the formation of which, according to Culvenor, Davies, and Heath (*loc. cit.*), is a characteristic property of compounds containing the ethylene sulphide ring. Reaction of (X) with 2 : 3-dimercaptopropanol under alkaline conditions would clearly give (XI).

It was expected that (X) would be formed by similar treatment of 2 : 3-bisacetylthio-propanol (XIII), but some difficulty was experienced in the synthesis of the latter. The reaction of 2 : 3-dibromopropanol with potassium thiolacetate in boiling ethanol gave a
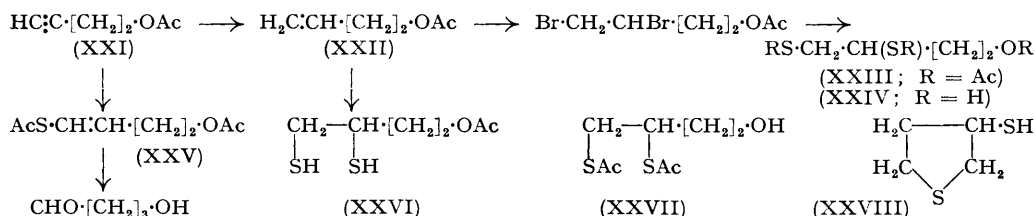
small quantity of what appeared to be a mixture of the required bisthiolacetate and its rearrangement product, but the main product was a polymer. Sjöberg (*Ber.*, 1942, **75**, 13) also attempted this reaction, but reported only its failure. When the dibromide was treated with thiolacetic acid in pyridine at 0°, only one bromine atom was replaced, and distillation of the product [probably (XIV)] effected substantial rearrangement to the thiol [probably (XV)]. The use of triethylamine brought about complete replacement of bromine, but intermolecular condensation apparently took place, since the product was almost entirely a polymer. However, acetylation of a solution of 2 : 3-dimercaptopropanol in two equivalents of aqueous sodium hydroxide, by shaking it with acetic anhydride, a method used for the acetylation of phenols (Chattaway, *J.*, 1931, 2495), gave a product which was mainly the required derivative. Treatment with sodium carbonate solution gave 3-acetylthiopropylene sulphide, identical with that obtained from the triacetyl compound.

Cyclisation of 2 : 3-dimercaptopropyl acetate (XVI) was effected under the same conditions, and gave 3-mercaptopropylene sulphide (XVII), together with a considerable quantity of polymer. Lazier and Signaigo (U.S.P. 2 396 597) had previously obtained (XVII) by thermal dehydration of 2 : 3-dimercaptopropanol, but had not proved its structure; this has now been effected by identification of the products of the acid-catalysed ring-fission. Heating of (XVII) with dilute hydrochloric acid gave a liquid with properties very similar to those of 2 : 3-dimercaptopropanol (XVIII), but it was shown to contain a small proportion of the isomeric 1 : 3-dimercaptopropan-2-ol (XIX) by desulphurisation with Raney nickel, oxidation of the product, and chromatographic separation of the 2 : 4-dinitrophenylhydrazones of the resulting carbonyl compounds; in this way some acetone 2 : 4-dinitrophenylhydrazone was detected in the presence of the main constituent, propaldehyde 2 : 4-dinitrophenylhydrazone. The formation of acetone provides conclusive proof of the structure (XVII), since (XX), the other possible dehydration or deacetylation product, could give only (XVIII) on hydrolysis. It is of interest that 2 : 3-dimercaptopropanol is the main product of the ring-fission, indicating a preferential opening of the sulphur–$C_{(1)}$ link, since Davies and Savige (*J.*, 1950, 317) have reported that when propylene sulphide is treated with hydrochloric acid it gives 2-chloropropanethiol, the bond between the sulphur and $C_{(2)}$ being broken. Nevertheless, the formation of some 1 : 3-dimercapto-propan-2-ol is of importance, because it indicates that a 1 : 3-dithiol can in certain circumstances arise from an acetylated 1 : 2-dithiol.

In order to determine to what extent the high reactivity of the 1-position in 2 : 3-dimercaptopropanol would be affected by the interposition of a methylene group, attention was next directed to the higher homologue, 3 : 4-dimercaptobutanol. Pavlic, Lazier, and Signaigo (*loc. cit.*) had obtained this dithiol by reaction of sodium hydrogen sulphide with 3 : 4-dibromobutanol, the latter being derived from but-3-en-1-ol, prepared, in poor yield, by the Grignard reaction of allyl iodide and formaldehyde. A better method appeared to be from but-3-yn-1-ol, readily available by reaction of sodium acetylide with ethylene oxide in liquid ammonia (Macallum, U.S.P. 2 125 384). Semi-hydrogenation of the butynyl acetate (XXI) in ethyl acetate solution over a palladium–charcoal catalyst gave but-3-en-1-yl acetate (XXII), which by addition of bromine and reaction of the dibromide with potassium thiolacetate in ethanol furnished triacetyl 3 : 4-dimercaptobutanol (XXIII); deacetylation with methanolic hydrogen chloride gave 3 : 4-dimercaptobutanol (XXIV). An alternative route, based on the addition of thiolacetic acid to (XXI), was also investigated, since this would be expected to give (XXIII) directly (cf. Bader, Cross, Heilbron, and Jones, *J.*, 1949, 619). The acetate was treated with excess of thiolacetic acid and a little ascaridole; heating for two hours at 100° gave mainly the mono-adduct, 4-acetylthiobut-3-en-1-yl acetate (XXV), the structure of which was confirmed by reaction with 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid, γ-hydroxybutaldehyde 2 : 4-dinitrophenylhydrazone being formed. Longer heating of the reactants, with either ascaridole or sulphuric acid catalyst, brought about some di-addition but no pure di-adduct could be separated. But-3-yn-1-ol itself reacted vigorously with thiolacetic acid, but no recognisable product could be isolated.
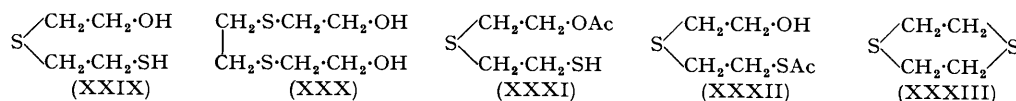
3 : 4-Dimercaptobutyl acetate (XXVI) and 3 : 4-bisacetylthiobutanol (XXVII) were

prepared from 3 : 4-dimercaptobutanol by methods similar to those used for the lower homologues. They were less reactive than their lower homologues, but with boiling aqueous sodium carbonate both gave some 3-mercaptothiophan (XXVIII), the properties

HC:C·[CH$_2$]$_2$·OAc $\longrightarrow$ H$_2$C:CH·[CH$_2$]$_2$·OAc $\longrightarrow$ Br·CH$_2$·CHBr·[CH$_2$]$_2$·OAc $\longrightarrow$

(XXI) (XXII) RS·CH$_2$·CH(SR)·[CH$_2$]$_2$·OR

(XXIII; R = Ac)
(XXIV; R = H)

AcS·CH:CH·[CH$_2$]$_2$·OAc

(XXV)

CHO·[CH$_2$]$_3$·OH

CH$_2$—CH·[CH$_2$]$_2$·OAc
| |
SH SH

(XXVI)

CH$_2$—CH·[CH$_2$]$_2$·OH
| |
SAc SAc

(XXVII)

H$_2$C———CH·SH
| |
H$_2$C CH$_2$
\ /
S

(XXVIII)

of which agreed with those recorded by Pavlic, Lazier, and Signaigo (*loc. cit.*) for a liquid obtained as a by-product in their preparation of 3 : 4-dimercaptobutanol; these authors suggested, but did not prove, the structure (XXVIII). This has now been done by selective hydrogenolysis, a solution of the compound in ethanol being heated for a short time with Raney nickel; the thiol group was preferentially reduced, and by interruption of the re-action at the appropriate time (indicated by estimation of thiol values) thiophan was obtained, and identified as its mercuric chloride complex. (The selective desulphurisation of mercaptothiazoles has been reported by Cook, Heilbron, and Levy, *J.*, 1947, 1598.)

In order to determine whether a six-membered ring could be formed by intramolecular deacetylation, a 1 : 5-hydroxy-thiol was required. That most readily accessible at the time was 2-hydroxy-2'-mercaptodiethyl sulphide (XXIX), which was prepared by the addition

S
/CH$_2$·CH$_2$·OH
\CH$_2$·CH$_2$·SH

(XXIX)

CH$_2$·S·CH$_2$·CH$_2$·OH
|
CH$_2$·S·CH$_2$·CH$_2$·OH

(XXX)

S
/CH$_2$·CH$_2$·OAc
\CH$_2$·CH$_2$·SH

(XXXI)

S
/CH$_2$·CH$_2$·OH
\CH$_2$·CH$_2$·SAc

(XXXII)

S
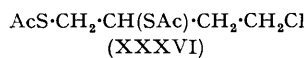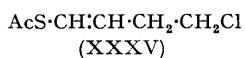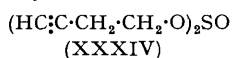/CH$_2$·CH$_2$\
\CH$_2$·CH$_2$/ S

(XXXIII)

of excess of ethanedithiol to ethylene oxide in ethanolic sodium ethoxide (cf. Owen and Smith, *loc. cit.*); a small proportion of 1 : 2-di-(2-hydroxyethylthio)ethane (XXX), pre-viously described by Bennett and Whincop (*J.*, 1921, **119**, 1860), was also formed in this reaction. Monoacetylation of (XXIX) with acetic anhydride in acetic acid containing a little sulphuric acid gave the *O*-acetate (XXXI), whilst acetylation of the sodium derivative of (XXIX) in aqueous solution gave mainly the *S*-acetyl compound (XXXII). Neither (XXXI) nor (XXXII) gave any dithian (XXXIII) by alkaline deacetylation, although the free hydroxy-thiol was readily cyclised by treatment with hydrochloric acid.

The formation of cyclic sulphides by intramolecular deacetylation has not previously been observed, and the reaction provides a new illustration of the influence of sulphur, compared with oxygen, on the reactivity of neighbouring groups. Cyclic oxides can be prepared by alkaline hydrolysis of toluene-*p*-sulphonates, methanesulphonates, nitrates, and sulphates (cf. Peat, *Adv. Carbohydrate Chem.*, 1946, **2**, 37), but not of acetates; this is usually explained by the ease with which the first four types of esters undergo alkyl–oxygen fission, whereas with acetates acyl–oxygen fission is the rule. Although in the present work cyclisation has been found to occur both with *O*- and with *S*-acetyl derivatives, there is little doubt that the cyclic sulphide is actually formed only from the former, and that when an *S*-acetyl compound [*e.g.*, (II) or (IV)] is treated with alkali it is first converted into the *O*-acetyl isomer [(I) or (V)] (unpublished results by Mr. J. S. HARDING). Ring-formation, therefore, must occur by removal of the acetoxy-group, *i.e.*, by the unusual alkyl–oxygen fission; this type of hydrolysis is known to be facilitated by electron-donating groups in the " alkyl " portion, and in the present instances the sulphur atom or atoms are clearly functioning in that way. It is noteworthy that the three- and five-membered sulphide rings are formed so easily, since the three- and five-membered oxide rings are those which are most readily formed by the alkaline hydrolysis of toluene-*p*-sulphonates, etc.

The greater stability towards hydrolysis shown by 3 : 4-dimercaptobutyl acetate com-pared with 2 : 3-dimercaptopropyl acetate is due to the interposition of the methylene group, which reduces the influence of the sulphur atoms on the linkage of the acetoxy-group to $C_{(1)}$, in general agreement with Bennett's conclusions on the effect of sulphur on the reactivity

of adjacent groups (*inter al.*, Bennett and Berry, *J.*, 1927, 1676). It would therefore be of interest to investigate the properties of the unknown 3 : 4-dimercaptobutyl chloride, in view of the high reactivity of the halogen in 2 : 3-dimercaptopropyl chloride and in 2 : 3-benzylidenedithiopropyl bromide (Miles and Owen, *J.*, 1950, 2938). Attempts to convert 3 : 4-dimercaptobutanol into the chloride by treatment with fuming hydrochloric acid, hydrogen chloride–zinc chloride in ether, or thionyl chloride, were unsuccessful, and a different method of approach was therefore investigated, involving the addition of thiolacetic acid to 4-chlorobut-1-yne. Reaction of but-3-yn-1-ol with thionyl chloride in cold pyridine gave di(but-3-ynyl) sulphite (XXXIV), but at 70°, in the presence of only a trace of pyridine (cf. Gerrard, *J.*, 1944, 85; Gerrard and French, *Nature*, 1947, **159**, 263), 4-chlorobut-1-yne was obtained in good yield; this reacted with thiolacetic acid, ascaridole being

$$(HC{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2SO \qquad AcS{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2Cl \qquad AcS{\cdot}CH_2{\cdot}CH(SAc){\cdot}CH_2{\cdot}CH_2Cl$$
$$\text{(XXXIV)} \qquad\qquad \text{(XXXV)} \qquad\qquad\qquad \text{(XXXVI)}$$

used as catalyst, to give a mixture of mono- and di-addition products. The lower-boiling fraction was shown to contain 1-acetylthio-4-chlorobut-1-ene (XXXV) by the formation of γ-chlorobutaldehyde on acid hydrolysis; the high-boiling material was mainly 3 : 4-bisacetylthiobutyl chloride (XXXVI). Hydrolysis of the latter with methanolic hydrogen chloride gave a product which probably contained 3 : 4-dimercaptobutyl chloride (since it gave 3-mercaptothiophan on treatment with alkali), but it could not be purified.

Although abnormal deacetylations have occurred more often under alkaline conditions, we have occasionally observed the formation of by-products when acetylated hydroxy-thiols have been boiled with N-methanolic hydrogen chloride, and in one instance (Evans, Fraser, and Owen, *loc. cit.*) a cyclic sulphide was isolated. It is well known that hydroxy-thiols undergo cyclisation and condensation to chain-polymers when they are treated with concentrated aqueous hydrochloric acid, the reactions occurring through sulphonium intermediates (Bell, Bennett, and Hock, *J.*, 1927, 1803; cf. Ray and Levine, *J. Org. Chem.*, 1937, **2**, 267; Bennett, *Trans. Faraday Soc.*, 1941, **37**, 794), and it is likely that this type of side reaction occurs to some extent even when the concentration of hydrogen chloride is quite small.

EXPERIMENTAL

(Except where otherwise stated, thiol values were determined by the method described in Part II, *J.*, 1949, 244; light petroleum refers to the fraction b. p. 40—60°.)

2-*Mercaptoethyl Acetate.*—To 2-mercaptoethanol (5 g.), containing a 10% solution of sulphuric acid in acetic acid (0·2 c.c.), acetic anhydride (6·8 g., 1 equiv.) was added during 10 minutes, the temperature being kept at *ca.* 40° by external cooling. The solution was then warmed in a water-bath at 60° for 1 hour, and finally left at room temperature for 20 hours. Ether (50 c.c.) was added, and the ethereal solution was washed three times with water and dried (NaHCO₃ and Na₂SO₄). Removal of the ether left a colourless liquid (8·2 g.), which on distillation gave a small low-boiling fraction and a main fraction of 2-mercaptoethyl acetate (5·5 g., 71%), b. p. 62—64°/16 mm., n_D^{20} 1·4612 (Found : thiol-S, 26·6. Calc. for $C_4H_8O_2S$: thiol-S, 26·7%). Nylen and Olsen (*loc. cit.*) give b. p. 52°/7 mm., n_D^{20} 1·4610.

The acetate (0·2 g.) was dissolved in 1 : 1 aqueous ethanol (20 c.c.), and 0·1N-sodium hydroxide (20 c.c.) was added. A white flocculent precipitate gradually formed, and there was a strong odour of ethylene sulphide. Under the same conditions, a solution of 2-mercaptoethanol remained clear and gave no ethylene sulphide.

trans-2-*Acetylthiocyclohexanol.*—Thiolacetic acid (7·8 g., 0·1 mol.) was added to *cyclo*hexene oxide (10 g., 0·1 mol.); a bright yellow colour appeared, but rapidly faded. After 60 hours at room temperature the mixture had become more viscous, and was distilled. trans-2-*Acetyl-thiocyclohexanol* (15 g., 84%), b. p. 72°/0·001 mm., n_D^{16} 1·5197, was thus obtained as a colourless liquid with a characteristic revolting odour (Found : S, 18·5. $C_8H_{14}O_2S$ requires S, 18·4%). Light absorption : max. 2340 Å, ε = 4500. Titration of a solution of the acetate in aqueous ethanol with iodine in the presence of only a trace of hydrochloric acid showed the presence of very little free thiol (Found : thiol-S, 0·5%). In N-hydrochloric acid, however, iodine continued to be taken up until a stable end-point was reached corresponding to the liberation of one free thiol group (Found : thiol-S, 18·5%); whether this was due to hydrolysis or to acyl migration was not established.

trans-2-*Mercaptocyclohexyl Acetate.*—trans-2-Acetylthio*cyclo*hexanol (12 g.) with acetic

acid (0·1 g.) was kept at 100° for 13 hours; there was a change in odour and a decrease in viscosity. Distillation gave *trans*-2-mercapto*cyclo*hexyl acetate (11 g.) b. p. 106—108°/15 mm., n_D^{16} 1·4897 (Found : thiol-S, 18·5. Calc. for $C_8H_{14}O_2S$: thiol-S, 18·4%). Culvenor, Davies, and Heath (*loc. cit.*) give b. p. 109°/15 mm.

Alkaline Hydrolysis of trans-2-*Mercapto*cyclo*hexyl Acetate.*—(i) The acetate (2 g.) in a solution of sodium hydroxide (1·0 g.) in 50% aqueous ethanol (10 c.c.) was set aside for 12 hours. Dilution with water (50 c.c.), extraction with chloroform (50 c.c.), and concentration of the dried (Na_2SO_4) extract gave a viscous liquid (1·3 g.), which on distillation gave a trace of *cyclo*hexene sulphide, b. p. *ca.* 70°/15 mm., and 2-*hydroxy*-2'-*mercaptodi*cyclo*hexyl sulphide* (0·3 g.), b. p. 150—160°/0·2 mm. (Found : S, 26·0; thiol-S, 13·3. $C_{12}H_{22}OS_2$ requires S, 26·0; thiol-S, 13·0%). The residue was a colourless glass. The hydroxy-thiol (0·12 g.) in ethanol (1 c.c.), 1-chloro-2 : 4-dinitrobenzene (0·10 g.) in ethanol (0·5 c.c.), and sodium hydroxide (0·02 g.) in water (0·5 c.c.) were mixed, heated under reflux for 5 minutes, and filtered hot. Removal of the solvent and chromatography of the residual oil on alumina, with benzene as eluent, gave 2-*hydroxy*-2'-(2 : 4-*dinitrophenylthio*)dicyclo*hexyl sulphide* (0·1 g.) which crystallised from ethanol in yellow prisms, m. p. 128° (Found : N, 6·9. $C_{18}H_{24}O_5N_2S_2$ requires N, 6·8%).

Acidification of the alkaline solution remaining from the chloroform extraction, and further extraction with chloroform, gave a mobile liquid (0·6 g.) (Found : thiol-S, 16·0%). A portion (0·5 g.), on reaction with sodium hydroxide and 1-chloro-2 : 4-dinitrobenzene, as above, gave 2 : 4-dinitrophenyl *trans*-2-hydroxy*cyclo*hexyl sulphide (0·55 g.), m. p. 135° after chromatography and recrystallisation from ethanol. Culvenor and Davies (*loc. cit.*) give m. p. 134—135°.

(ii) *trans*-2-Mercapto*cyclo*hexyl acetate (3·5 g.) was added to a warm solution of sodium hydrogen carbonate (2·0 g.) in water (40 c.c.), which was then steam-distilled at 60°/150 mm. (under these conditions the reagent is effectively aqueous sodium carbonate). A colourless oil distilled over with the first drops of water, and continued to be formed for 30 minutes. The distillate was extracted with light petroleum, and the extract was dried (Na_2SO_4) and concentrated. Distillation of the residue (2·2 g.) gave *cyclo*hexene sulphide (1·6 g., 70%), b. p. 65—70°/15 mm., n_D^{15} 1·5245, and unchanged acetate (0·35 g., 10%), b. p. 75°/2 mm., n_D^{15} 1·4894. Culvenor, Davies, and Pausacker (*loc. cit.*) give b. p. 67—68°/16 mm., n_D^{20} 1·5309 for *cyclo*hexene sulphide.

trans-2-Mercapto*cyclo*hexanol gave no *cyclo*hexene sulphide when similarly treated.

Alkaline Hydrolysis of trans-2-*Acetylthio*cyclohexanol.—The compound (0·5 g.) was treated with aqueous sodium hydrogen carbonate in the same way, and gave *cyclo*hexene sulphide (0·2 g.), b. p. 60—70°/15 mm., n_D^{15} 1·5232.

Alkaline Hydrolysis of the Triacetyl Derivative of 2 : 3-*Dimercaptopropanol.*—(i) The triacetyl derivative (16 g.) (Evans, Fraser, and Owen, *J.*, 1949, 248) was made up to 100 c.c. with 20% aqueous sodium hydroxide and shaken in a stoppered bottle. After 50 hours the maximum thiol value (57% of theory) was attained, and the solution was poured into 5N-hydrochloric acid (120 c.c.), with cooling. The resultant emulsion was extracted three times with ether, the extract was dried (Na_2SO_4), and the ether was removed by distillation. Fractionation of the residue (5 g.) gave : (1) 1·6 g., b. p. 71—75°/1 mm., n_D^{15} 1·5723 to 1·5733; (2) 1·1 g., b. p. 150—160°/0·001 mm., n_D^{15} 1·6190; (3) a viscous residue (2·3 g.). Constant ether-extraction of the aqueous solution for 12 hours gave a further 1·1 g., n_D^{15} 1·5722.

Fraction 1 was 2 : 3-dimercaptopropanol (Found : thiol-S, 51·2. Calc. for $C_3H_8OS_2$: thiol-S, 51·6%). A portion (0·2 g.) was dissolved in water (20 c.c.), Raney nickel (*ca.* 5 g.) was added, and the suspension was heated on the steam-bath for 4 hours. The nickel was removed by filtration, and the filtrate was boiled in a distillation flask during the addition of a 20% solution of potassium dichromate in 20% aqueous sulphuric acid. The distillate was collected in aqueous 2 : 4-dinitrophenylhydrazine sulphate, and gave propaldehyde 2 : 4-dinitrophenyl-hydrazone (0·1 g.), m. p. 155°, which was shown to be homogeneous by chromatography on alumina.

Fraction 2 was 3-*hydroxy*-2 : 2' : 3'-*trimercaptodipropyl sulphide* (Found : S, 55·2; thiol-S, 40·4. $C_6H_{14}OS_4$ requires S, 55·6; thiol-S, 41·8%). A portion (0·4 g.) was dissolved in acetone (5 c.c.) and hydrogen chloride was passed in for 1 minute. Heat was evolved and after 10 minutes potassium carbonate was added to neutralise the acid and to dry the solution. Removal of acetone from the filtered solution left a semi-solid residue. Trituration with ethanol gave a white solid (0·1 g., m. p. *ca.* 110°), which gave the pure *diisopropylidene* derivative, m. p. 132°, after recrystallisation from methanol (Found : S, 41·5. $C_{12}H_{22}OS_4$ requires S, 41·3%).

(ii) The triacetyl derivative (1·0 g.) of 2 : 3-dimercaptopropanol was added to a warm solution of sodium hydrogen carbonate (1·1 g.) in water (20 c.c.), and the reaction mixture was

steam-distilled at 60°/150 mm. for 3 hours, a colourless oil passing over with the distillate. This was extracted with light petroleum, and the extracts on evaporation gave a mobile liquid with a sweet but obnoxious odour, which on distillation furnished 3-*acetylthiopropylene sulphide* (0·5 g., 80%), b. p. 125°/40 mm., n_D^{18} 1·5525 (Found : S, 43·05; thiol-S, nil. $C_5H_8OS_2$ requires S, 43·25%). Light absorption : max. 2290 Å, ε = 3500. Treatment of this sulphide (0·2 g.) with methyl iodide (5 g.) for 2 weeks at room temperature gave a semi-solid product which on trituration with acetone furnished fine white needles (50 mg.), m. p. 205—210°. Recrystallisation from dry ethanol gave trimethylsulphonium iodide, m. p. 212°. Culvenor, Davies, and Heath (*loc. cit.*) give m. p. 215°.

2 : 3-*Bisacetylthiopropanol.*—(i) 2 : 3-Dibromopropanol (10 g.) was dissolved in dry pyridine (40 c.c.), and the solution was cooled to −5°. Thiolacetic acid (8·4 g.) was added dropwise, with stirring. After 64 hours at 0°, when some pyridine salt had crystallised out, the solution was poured into water (200 c.c.). Extraction with chloroform, and distillation of the extract (7·5 g.) showed that a mixture had been obtained, including an involatile polymer (3 g.). The higher-boiling fraction (0·8 g.) was re-distilled, and gave a mobile liquid, b. p. 60—62°/0·1 mm., n_D^{20} 1·5198, probably a mixture of 72% of *O*- and 28% of *S*-acetyl-2-bromo-3-mercaptopropanol (Found : S, 15·1; thiol-S, 10·9; Br, 37·8. Calc. for $C_5H_9O_2SBr$: S, 15·0; Br, 37·5%).

(ii) 2 : 3-Dimercaptopropanol (10 g.) was dissolved in a solution of sodium hydroxide (7·5 g.) in water (100 c.c.). The solution was cooled to 0°, and acetic anhydride (20 g.) was added in one portion; the mixture was vigorously stirred for 10 minutes and then allowed to separate into two layers. The upper aqueous portion was discarded, and the oil was washed twice with an equal volume of light petroleum, and then diluted with benzene, dried ($MgSO_4$), and evaporated under reduced pressure below 40° to give a viscous liquid (11·1 g.) consisting mainly of 2 : 3-bisacetylthiopropanol, containing a small proportion of free thiol (Found : Ac, 41·2; thiol-S, 3·1. Calc. for $C_7H_{12}O_3S_2$: Ac, 41·3%). Light absorption : max. 2300 Å, ε = 7800. Distillation of a portion at 100° (bath)/0·0001 mm. resulted in partial isomerisation, and gave a less viscous liquid (Found : thiol-S, 12·1%. Calc. for complete rearrangement : thiol-S, 15·4%).

Alkaline Hydrolysis of 2 : 3-Bisacetylthiopropanol.—The undistilled material (3 g.) was added to a warm solution of sodium hydrogen carbonate (4 g.) in water (40 c.c.) and steam-distilled at 60°/150 mm. for an hour. The distillate, which contained an upper oily layer, was extracted with light petroleum; distillation of the dried ($MgSO_4$) extract gave 3-acetylthiopropylene sulphide (1·2 g., 55%), b. p. 120°/35 mm., n_D^{23} 1·5500.

Alkaline Hydrolysis of 2 : 3-Dimercaptopropyl Acetate.—The acetate (7·2 g.) (Pavlic, Lazier, and Signaigo, *loc. cit.*) was added to a warm solution of sodium hydrogen carbonate (4 g.) in water (50 c.c.), and steam-distilled at 60°/150 mm., a light oil coming over with the first drops of distillate. After 1 hour, when no more oil was being collected, the distillate was extracted with light petroleum. The extract was dried (Na_2SO_4) and evaporated, and the residue was distilled, to give 3-mercaptopropylene sulphide (1·1 g., 27%), b. p. 66—67°/20 mm., n_D^{18} 1·5810 (Found : thiol-S, 31·2. Calc. for $C_3H_6S_2$: thiol-S, 30·2%). B.P. 597 368 gives b. p. 77°/30 mm., n_D^{25} 1·5799. Addition of phenyl *iso*cyanate (0·13 g.) to the thiol (0·1 g.) gave, after 2 hours, a *phenylurethane* (0·2 g.), m. p. 102° after recrystallisation from light petroleum (b. p. 60—80°) (Found : N, 6·5. $C_{10}H_{11}ONS_2$ requires N, 6·2%).

The steam-involatile material (3 g.) was a mixture of high-boiling polymers, from which no homogeneous product could be obtained.

Acid Ring-fission of 3-Mercaptopropylene Sulphide.—The mercapto-sulphide (1·0 g.), suspended in N-hydrochloric acid (30 c.c.) and acetic acid (10 c.c.), was heated on the steam-bath for 3 hours, most of the oil dissolving. Extraction with benzene gave a viscous liquid (0·9 g.), distillation of which gave a more mobile liquid (0·4 g.), b. p. 70—75°/1 mm., n_D^{19} 1·5710 (Found : thiol-S, 50·6. Calc. for $C_3H_8OS_2$: S, 51·6%). This mixture of 2 : 3-dimercaptopropanol and 1 : 3-dimercaptopropan-2-ol (0·3 g.) in water (20 c.c.) was heated on the steam-bath for 4 hours with Raney nickel (*ca.* 5 g.). The nickel was removed by filtration and the hot filtrate was oxidised by the addition of acid potassium dichromate solution. Distillation into aqueous 2 : 4-dinitrophenylhydrazine sulphate gave an orange precipitate (200 mg.) which was collected and chromatographed on alumina, with benzene as eluent; this separated acetone 2 : 4-dinitrophenylhydrazone (14 mg.), m. p. and mixed m. p. 126°, from the propaldehyde 2 : 4-dinitrophenylhydrazone (150 mg.), m. p. and mixed m. p. 156—157°.

But-3-yn-1-yl acetate, b. p. 77—78°/60 mm., n_D^{22} 1·4255 (Found : C, 64·4; H, 7·3. Calc. for $C_6H_8O_2$: C, 64·3; H, 7·2%), was prepared by acetylation of but-3-yn-1-ol with acetic anhydride and pyridine (cf. Jones, Shen, and Whiting, *J.*, 1950, 230).

Addition of Thiolacetic Acid to Butynyl Acetate.—Thiolacetic acid (13 g.) and ascaridole (0·05 c.c.) were added to butynyl acetate·(5 g.). There was no evolution of heat, and the mixture was heated on the steam-bath for 2 hours. The unchanged materials (15 g.) were removed by distillation at 50 mm., and the red liquid residue was fractionated through a short column. The lower-boiling material (2·3 g.), b. p. 100—103°/5 mm., n_D^{25} 1·4985, was mainly 4-acetylthiobut-3-en-1-yl acetate (Found : S, 18·3. Calc. for $C_8H_{12}O_3S$: S, 17·1%). Light absorption : max. 2450, 2510 Å; ε = 6600, 7100. A portion (0·6 g.) was dissolved in a solution of 2 : 4-dinitrophenylhydrazine (1 g.) in methanol (20 c.c.) containing sulphuric acid (1 g.) and the solution was heated under reflux until no more hydrogen sulphide was evolved (8 hours). On cooling and addition of water, a crude solid (0·75 g.), m. p. 100—104°, was obtained. Recrystallisation from ethanol gave γ-hydroxybutaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 113° (corr.) (Found : N, 20·9. Calc. for $C_{10}H_{12}O_5N_4$: N, 20·9%). Light absorption : max. 3560 Å, ε = 21,400. Adkins and Krsek (*J. Amer. Chem. Soc.*, 1948, **70**, 383) gave m. p. 178—179°, but this was a misprint for 108—109° (private communication).

Triacetyl Derivative of 3 : 4-Dimercaptobutanol.—A solution of but-3-yn-1-yl acetate (50 g.) in ethyl acetate (50 c.c.), with a 10% palladium–charcoal catalyst (1·2 g.), was shaken with hydrogen at atmospheric pressure until the required volume (10·95 l.) was taken up (4 hours). Removal of the catalyst by filtration, concentration, and distillation of the residue, gave but-3-en-1-yl acetate (49·7 g.), b. p. 58—59°/60 mm., n_D^{20} 1·4118 (Found : C, 63·0 ; H, 8·9. Calc. for $C_6H_{10}O_2$: C, 63·2 ; H, 8·8%). Pariselle (*Ann. Chim. Phys.*, 1911, [viii], **24**, 324) gives b. p. 125°, n_D^{15} 1·411.

Bromine (35 g.) in carbon tetrachloride (20 c.c.) was added dropwise to a solution of the butenyl acetate (25 g.) in carbon tetrachloride (50 c.c.) at 0°. 3 : 4-Dibromobutyl acetate (46 g., 55%) was thus obtained, having b. p. 84—85°/1 mm., n_D^{18} 1·5104. Pariselle (*loc. cit.*) records b. p. 135°/16 mm., n_D^{18} 1·508.

The dibromide (45 g.), potassium thiolacetate (41 g.), and thiolacetic acid (0·5 c.c.) in ethanol (200 c.c.) were heated under reflux for 6 hours. Most of the solvent was then removed under reduced pressure, and the residue was extracted with ether. The extracts were washed with water, dried (Na_2SO_4) and evaporated to give 3 : 4-bisacetylthiobutyl acetate (37 g., 80%), b. p. 110—112°/0·0001 mm., n_D^{D} 1·5150 (Found : C, 44·6 ; H, 6·05 ; S, 23·8. $C_{10}H_{16}O_4S_2$ requires C, 45·4 ; H, 6·1 ; S, 24·3%). Light absorption : max. 2300 Å, ε = 8700.

3 : 4-Dimercaptobutanol.—The triacetyl compound (45 g.) in 2% methanolic hydrogen chloride (200 c.c.) was heated under reflux for 4 hours, and the solvent was removed by distillation. The residue (30 g.) was shaken with water (600 c.c.), and the insoluble dark red oil (3·5 g.) was discarded. Extraction with light petroleum (100 c.c.) removed a further quantity (1·5 g.) of orange-red material. Further extraction with benzene (3 × 100 c.c.) gave almost pure 3 : 4-dimercaptobutanol as a pale yellow liquid (12 g.), b. p. 77—78°/0·0001 mm., n_D^{18} 1·5593 (Found : thiol-S, 45·8%). Finally, extraction with ether (3 × 200 c.c.) gave a colourless viscous oil (5 g.), distillation of which gave the pure dithiol, b. p. 70—71°/0·0001 mm., n_D^{23} 1·5572 (Found : thiol-S, 46·3. Calc. for $C_4H_{10}OS_2$: thiol-S, 46·4%). Pavlic, Lazier, and Signaigo (*loc. cit.*) give b. p. 96—97°/1 mm., n_D^{25} 1·5583.

The dithiol (0·7 g.) in ethanol (15 c.c.), sodium hydroxide (0·4 g.) in water (3 c.c.), and 1-chloro-2 : 4-dinitrobenzene (2·0 g.) in ethanol (10 c.c.) were mixed. Heat was evolved and the solution became orange, red, then brown, and an oil was deposited on the walls of the flask. The mixture was heated under reflux for 5 minutes, and then filtered hot. On cooling and dilution with water, a crude solid (0·35 g.) was obtained. Recrystallisation from 5 : 1 methanol-nitrobenzene gave 3 : 4-di-(2 : 4-dinitrophenylthio)butanol, bright yellow needles, m. p. 183° (Found : C, 41·0 ; H, 2·9 ; N, 11·7. $C_{16}H_{14}O_9N_4S_2$ requires C, 40·9 ; H, 3·0 ; N, 11·9%).

3 : 4-Dimercaptobutyl Acetate.—Acetic anhydride (7·8 g.) was added in small portions to the dithiol (10 g.) containing 0·2 c.c. of a 10% solution of sulphuric acid in acetic acid, the temperature being kept between 30° and 40°. The solution was then warmed at 60° for 1 hour and left at 20° for 20 hours. Ether was added, and the solution was washed with water, dried ($NaHCO_3$ and $MgSO_4$), and evaporated to an oil (13·5 g.). Fractionation gave 3 : 4-dimercaptobutyl acetate (4 g.), b. p. 65—66°/0·0001 mm., n_D^{20} 1·5208 (Found : S, 35·5 ; thiol-S, 35·2. $C_6H_{12}O_2S_2$ requires S, 35·6%). Light absorption : no high-intensity max. above 2200 Å.

3 : 4-Bisacetylthiobutanol (with J. S. HARDING).—Acetic anhydride (5 g.) was added, with shaking and cooling, to a solution of 3 : 4-dimercaptobutanol (3 g.) and sodium hydroxide (1·75 g.) in water (25 c.c.) at 0°. After 10 minutes the lower layer was removed and washed twice with light petroleum, the washings being rejected ; the oil was then diluted with benzene, dried ($MgSO_4$), and evaporated below 40° under reduced pressure. The product contained some

triacetyl derivative (Found : 2·4 acetyl groups per mol.) and was therefore dissolved in 5 volumes of methanol and extracted several times with light petroleum. Evaporation of the methanolic solution below 40° gave an oil which was essentially the required di-*S*-acetyl derivative, containing only a small proportion of free thiol and triacetyl derivative (Found : S, 27·2; thiol-S, 2·2; Ac, 40·2. Calc. for $C_8H_{14}O_3S_2$: S, 28·8; Ac, 38·7%). Light absorption : max. 2300 Å, ε = 7550.

Alkaline Hydrolysis of the Acetyl Derivatives of 3 : 4-Dimercaptobutanol (with J. S. HARDING).
—(i) 3 : 4-Dimercaptobutyl acetate (2 g.) was boiled under reflux for 20 minutes with a solution of sodium hydrogen carbonate (2·7 g.) in water (80 c.c.); the mixture was then distilled in steam until no more oil was collected. Extraction of the distillate with light petroleum, and evaporation of the dried (MgSO₄) extracts, gave 0·3 g., which on distillation furnished 3-*mercapto-thiophan* (0·2 g.), b. p. 95°/30 mm., n_D^{20} 1·5780 (Found : C, 40·0; H, 6·7; S, 52·4; thiol-S, 26·3. $C_4H_8S_2$ requires C, 40·0; H, 6·7; S, 53·4; thiol-S, 26·7%). Treatment with phenyl *iso*cyanate for an hour at ordinary temperature gave the *phenylurethane*, which crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 106° (Found : C, 55·8; H, 5·6; N, 5·9. $C_{11}H_{13}ONS_2$ requires C, 55·2; H, 5·5; N, 5·9%).

(ii) Similar treatment of 3 : 4-bisacetylthiobutanol (1·2 g.) gave 3-mercaptothiophan (0·1 g.), b. p. 85—90°/20 mm., n_D^{19} 1·5790.

(iii) Triacetyl 3 : 4-dimercaptobutanol (5 g.) was boiled under reflux for 4 hours with sodium hydrogen carbonate (15 g.) in water (40 c.c.). Steam-distillation, and isolation as before, gave 3-mercaptothiophan (0·25 g.), b. p. 93°/25 mm., n_D^{22} 1·5760.

Partial Desulphurisation of 3-Mercaptothiophan.—The compound (0·35 g.) was dissolved in ethanol (30 c.c.) and Raney nickel (1 g.) was added. After 15 minutes' heating under reflux, a sample (0·5 c.c.) was withdrawn, filtered, acidified with hydrochloric acid, and titrated with iodine; the thiol value indicated 75% removal of the SH group. After a further 5 minutes (when the titration indicated 80% reaction) the solution was cooled and filtered. The filtrate was diluted with an equal volume of water, and a solution of mercuric chloride (1 g.) in water (20 c.c.) was added. The precipitate was collected and dried (0·45 g.; m. p. 120—125°). Recrystallisation from aqueous alcohol gave white needles of the mercuric chloride complex of thiophan, m. p. and mixed m. p. 123—125°.

2-Hydroxy-2'-mercaptodiethyl Sulphide.—Ethylene oxide (3·5 g.) was dissolved in ethanol (100 c.c.) at 0° contained in a wide-mouthed bottle, and sodium (0·2 g.) was added. A test-tube containing ethane-1 : 2-dithiol (9 g.) was supported in the bottle, which was then securely stoppered, cooled in ice, and inverted, and the contents were mixed. After a short time the solution became warm. After 14 hours at room temperature, the bottle was opened, and solid carbon dioxide was added to neutralise the sodium. The solution was concentrated, ether was added to the residue, and the sodium salts were removed by filtration. Evaporation of the ether, and fractionation of the residual oil (8 g.), separated the 2-*hydroxy-2'-mercaptodiethyl sulphide* (4·2 g., 38%), b. p. 106°/0·5 mm., n_D^{19} 1·5622 (Found : S, 46·2; thiol-S, 23·3. $C_4H_{10}OS_2$ requires S, 46·4; thiol-S, 23·2%), from the 1 : 2-di-(2-hydroxyethylthio)ethane (1·0 g., 14%), b. p. 170°/0·5 mm., white plates, m. p. 64° after one recrystallisation from ether. Bennett and Whincop (*J.*, 1921, **119**, 1860) also give m. p. 64°.

Alkaline Hydrolysis of the O- and the S-Acetyl Derivative of 2-Hydroxy-2'-mercaptodiethyl Sulphide.—The hydroxy-thiol (3·5 g.) was acetylated with acetic anhydride (2·7 g.) and a 10% solution of sulphuric acid in acetic acid (0·2 c.c.) in the same way as for 2-mercaptoethanol, but the reaction did not proceed with the same degree of selectivity. Careful fractionation, however, gave the O-*acetate* (0·8 g.), b. p. 98—100°/0·5 mm., n_D^1 1·5269 (Found : S, 36·6; thiol-S, 18·0. $C_6H_{12}O_2S_2$ requires S, 35·6; thiol-S, 17·8%). This product (0·6 g.) was dissolved in a solution of sodium hydroxide (0·5 g.) in water (10 c.c.), and steam-distilled for an hour. The solution remained homogeneous, and the distillate was clear and odourless.

(With J. S. HARDING). Acetic anhydride (1·05 g.) was added to a solution of the hydroxy-thiol (1·4 g.) and sodium hydroxide (0·4 g.) in water (15 c.c.) at 0°. After 10 minutes, extraction with benzene and evaporation of the dried (Na₂SO₄) extracts gave an oil, which on distillation furnished the S-*acetyl* derivative (0·93 g.), b. p. 108—110°/0·4 mm., n_D^{20} 1·5338 (Found : C, 39·9; H, 6·8; thiol S, 0·9. $C_6H_{12}O_2S_2$ requires C, 40·0; H, 6·7%). Light absorption : max. 2270, 2360 Å; ε = 4670, 3400. Treatment with alkali, as for the O-acetate, again gave no dithian.

Dithian from 2-Hydroxy-2'-mercaptodiethyl Sulphide.—The hydroxy-thiol (0·5 g.) was added to hydrochloric acid (15 c.c.; d 1·16). It dissolved immediately, but the solution rapidly became cloudy, and a flocculent precipitate was formed. After 12 hours this was collected, washed with

3 H

water, and dried (0·2 g.; m. p. 65—80°). It contained halogen, and was involatile at 60°/15 mm. though after such heating it showed m. p. 75—80°. The original aqueous acid filtrate on steam-distillation gave dithian (0·03 g.) and involatile polymer (0·25 g.); the latter, on crystallisation from ethanol, gave a main fraction, m. p. 78—80°, apparently identical with that described above (Found : S, 46·9; Cl, 9·1%). Depolymerisation was effected by heating 0·2 g. in phenol (1 g.) at 160—180° for 3 hours in a sealed tube; hydrogen chloride was liberated. The product was washed with sodium hydroxide, and the insoluble residue (0·15 g.) on steam-distillation gave dithian (0·07 g.), m. p. 110°.

4-Chlorobut-1-yne.—(i) But-3-yn-1-ol (4·6 g.) was dissolved in pyridine (50 c.c.), and the solution was cooled to 0°. Thionyl chloride (8 g.) was added slowly with constant shaking, the temperature being kept below 5°. Pyridine hydrochloride separated out almost immediately. After 1 hour at 0°, ice was added, followed by cold 2N-sulphuric acid. Extraction with ether, and distillation of the extracted material, gave a small quantity of low-boiling liquid, followed by *dibut-3-ynyl sulphite* (5·2 g., 85%), b. p. 124—126°/15 mm., n_D^{15} 1·4750 (Found : S, 17·2. $C_8H_{10}O_3S$ requires S, 17·2%). The liquid was soluble in warm 2N-sodium hydroxide, and on acidification of the solution sulphur dioxide was evolved.

(ii) Thionyl chloride (9 g.) was added to but-3-yn-1-ol (5·4 g.), containing a trace of pyridine (*ca.* 0·1 c.c.), cooled in ice. The mixture was then heated under reflux on a water-bath at 70° for 3 hours. Direct distillation gave a small quantity of thionyl chloride, and then *4-chlorobut-1-yne* (5·2 g., 76%), b. p. 78°, n_D^{16} 1·4420 (Found : C, 54·3; H, 5·9. C_4H_5Cl requires C, 54·3; H, 5·7%).

Addition of Thiolacetic Acid to 4-Chlorobut-1-yne.—(i) Thiolacetic acid (6 g.) was added to 4-chlorobut-1-yne (1·8 g.) containing ascaridole (0·1 c.c.). When the mixture was warmed to 30°, a vigorous exothermic reaction began; when this had subsided, the product was heated under reflux on the steam-bath for 1 hour, and excess of thiolacetic acid (2·8 g.) was removed by distillation at 100 mm. The residue was distilled and gave a lower-boiling fraction (2·5 g.), b. p. 79—80°/2 mm., n_D^{15} 1·5287, which was a mixture of the mono- and di-adduct (Found : S, 24·7; Cl, 16·6. Calc. for a mixture of C_6H_9OClS 27% and $C_8H_{13}O_2ClS_2$ 73% : S, 24·7; Cl, 16·5%). Light absorption : max. 2510 Å, $E_{1\,cm.}^{1\%}$ 425.

This product (1 g.) was added to a solution of 2 : 4-dinitrophenylhydrazine (2 g.) in methanol (30 c.c.), containing sulphuric acid (1·3 g.), and boiled under reflux until no more hydrogen sulphide was evolved (5 hours). γ-Chlorobutaldehyde 2 : 4-dinitrophenylhydrazone separated from the cooled solution; after recrystallisation from methanol it formed pale orange plates, m. p. 134°. Paul (*Compt. rend.*, 1942, **215**, 303) gives m. p. 134—135°.

(ii) Thiolacetic acid (14 g.) was added to 4-chlorobut-1-yne (4·2 g.) containing ascaridole (0·2 c.c.), and the mixture was heated on the steam-bath for 3 hours. The excess of thiolacetic acid (6·8 g.) was removed, and the residue was distilled. The lower-boiling material (4·9 g.), b. p. 75—85°/1·5 mm., n_D^{15} 1·5253—1·5294, contained some mono-adduct (see above); the higher-boiling fractions (4 g.), b. p. 108—111°/0·2 mm., were redistilled and gave substantially pure 3 : 4-*bisacetylthiobutyl chloride*, b. p. 92°/0·0001 mm., n_D^{15} 1·5392 (Found : S, 27·4; Cl, 14·1. $C_8H_{13}O_2ClS_2$ requires S, 26·6; Cl, 14·7%). Light absorption : Max. 2280, 2320 Å; ε = 9100. The high sulphur and low chlorine analysis was probably caused by the presence of a small proportion of 1 : 3 : 4-trisacetylthiobutane, formed by slow reaction of the halogen with thiolacetic acid; benzyl chloride, heated for 72 hours at 100° with an equal weight of thiolacetic acid, gave 5% of benzyl thiolacetate, b. p. 105°/12 mm., n_D^{16} 1·5612.

3-Mercaptothiophan from 3 : 4-Bisacetylthiobutyl Chloride.—The bisthiolacetate (6 g.) was heated under reflux in 2% methanolic hydrogen chloride (60 c.c.) for 2·5 hours. The solvent was removed on the steam-bath, and the product was distilled, to give a pale orange oil (1·1 g.), b. p. 60—75°/0·2 mm., n_D^{16} 1·5708; this product (1·0 g.) was added to a warm solution of sodium hydrogen carbonate (0·6 g.) in water (20 c.c.), and steam-distilled at 60°/150 mm., a light oil being collected in the distillate. This was extracted with light petroleum, and on distillation gave 3-mercaptothiophan (0·3 g.), b. p. 78°/15 mm., n_D^{16} 1·5750 (Found : thiol-S, 26·1. Calc. for $C_4H_8S_2$: thiol-S, 26·7%), characterised as the phenylurethane, m. p. and mixed m. p. 106°.