292. *Experiments with Thioacetals and Related Substances. Part II.*
The Reaction between α-*Bromopropaldehyde Diethylacetal and Ethylthiol.*

By Eugene Rothstein.

As a consequence of the hypothesis advanced in Part I (preceding paper) it follows that an atom or group which forms a stable anion should be easily eliminated from a molecule in which it was in a β-position to an alkylthio-group. This is confirmed by the instability of the halogen atom in β-*bromo-*αα-*bis(ethylthio)propane*, and by the easy removal of an ethylthio-group from ααβ-tris(ethylthio)propane, yielding αα- or αβ-bis-(ethylthio)-Δ^α-propene according to the conditions of the experiment. In similar circumstances, ααγ-*tris(ethylthio)propane* is stable.

THE experiments described in the previous paper show that, unlike γ-chloro-αα-bis(ethyl-thio)propane, where the halogen atom, in the absence of alkali, is relatively stable, βγ-di-bromo-αα-bis(ethylthio)propane eliminated hydrogen bromide on standing, and it appeared that any β-substituted thioacetal might easily lose the substituent in those cases where the latter could exist as a negative ion. A simple example is β-bromo-αα-bis(ethylthio)-propane, $CH_3 \cdot CHBr \cdot CH(SEt)_2$, obtainable from the corresponding acetal and ethylthiol; the product so obtained not only confirms the above suggestion but provides further evidence of the labile nature of similar types of β-substituents. The experimental results are summarised below.

1. When α-bromopropaldehyde diethylacetal is condensed with ethylthiol, there results a bis-sulphide which spontaneously loses hydrogen bromide on standing. Oxidation of this product yields a mixture of αα-bis(ethylsulphonyl)-Δ^α-propene, $CH_3 \cdot CH{:}C(SO_2Et)_2$

(I), and αβ-*bis(ethylsulphonyl)*-Δ*ᵅ*-*propene*, $CH_3 \cdot C(SO_2Et){:}CH(SO_2Et)$ (II). The same results are observed when α-bromopropaldehyde is used instead of its acetal.

2. If the above reaction mixture is distilled under reduced pressure, hydrogen bromide is evolved and the main product is αβ-*bis(ethylthio)*-Δ*ᵅ*-*propene*, $CH_3 \cdot C(SEt){:}CH(SEt)$ (III), which on oxidation gives (II), and is unchanged when boiled with potassium *tert.*-butoxide.

3. Boiling a xylene solution of the reaction mixture with anhydrous potassium carbonate furnishes ααβ-*tris(ethylthio)propane*, $CH_3 \cdot CH(SEt) \cdot CH(SEt)_2$ (IV), in 72% yield. This substance, which distils without decomposition, has also been made by an independent synthesis. Its structure is confirmed by boiling with aqueous mercuric chloride, whereby the two α-ethylthio-groups are lost and α-*ethylthiopropaldehyde*, $CH_3 \cdot CH(SEt) \cdot CHO$, results.

4. When the above tris-sulphide is oxidised, it is converted into a mixture of αα- and αβ-bis(ethylsulphonyl)propene (I and II). On the other hand, ααγ-*tris(ethylthio)propane*, $SEt \cdot CH_2 \cdot CH_2 \cdot CH(SEt)_2$, which has also been synthesised, affords ααγ-*tris(ethylsulphonyl)*-*propane*, $CH_2(SO_2Et) \cdot CH_2 \cdot CH(SO_2Et)_2$, on oxidation.

5. αα-Bis(ethylthio)-Δ*ᵅ*-propene, $CH_3 \cdot CH{:}C(SEt)_2$ (V), is produced when the tris-sulphide (IV) is boiled with potassium *tert.*-butoxide.
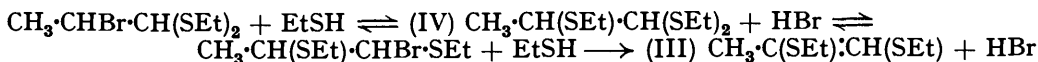
6. That interchange of ethylthio-groups or their migration does not take place in the above reactions was shown by the synthesis of αα-*bis(ethylthio)*-β-n-*butylthiopropane*, $CH_3 \cdot CH(SBu) \cdot CH(SEt)_2$ (VI), followed by reactions similar to those in paragraphs 4 and 5. Oxidation yielded a mixture of the sulphone (I) and α-*ethylsulphonyl*-β-n-*butylsulphonyl*-Δ*ᵅ*-*propene*, $CH_3 \cdot C(SO_2Bu){:}CH(SO_2Et)$ (VII), and the action of boiling potassium *tert.*-butoxide resulted in formation of the bis-sulphide (V) together with potassium butylthiol.

In retrospect it is evident that for the molecule of the ααβ-tris-sulphide (and similarly with the necessary alterations for the β-bromobis-sulphide) resonance can occur between valency structures such as
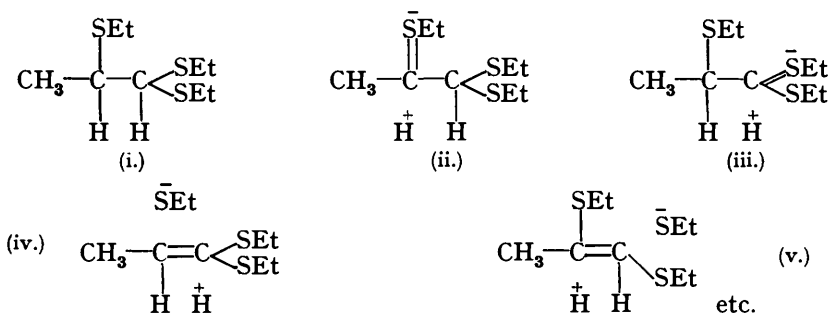
The preferential elimination of the β-group when the substance is boiled with alkoxide takes place because of the greater contribution of the structure (iii) (two thioacetal groups present and therefore two canonical structures) compared with that of (ii) (only one thioacetal group) to the final state of the molecule.* Furthermore, these eliminations cannot be dependent on a mechanism involving the sharing of the lone electrons on the sulphur atom (+ *M* effect; cf. Ingold, *Chem. Reviews*, 1934, **15**, 242), because in the dialkyl-β-chloropropylamines, $CH_3 \cdot CHCl \cdot CH_2 \cdot NR_2$, where such a mechanism might be expected to operate, alcoholic alkali causes substitution only (Ingold and Rothstein, J., 1931, **1666**). The +*M* effect would no doubt promote the ionisation of the halogen atom, but simultaneously it prevents the release of the α-hydrogen atom and no olefinic derivative is therefore formed.
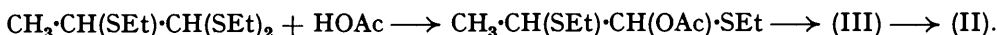
Although experimental difficulties prevent confirmatory evidence, the production of the various substances from β-bromo-αα-bis(ethylthio)propane may be explained by the following scheme :

$$CH_3 \cdot CHBr \cdot CH(SEt)_2 + EtSH \rightleftharpoons (IV)\ CH_3 \cdot CH(SEt) \cdot CH(SEt)_2 + HBr \rightleftharpoons$$
$$CH_3 \cdot CH(SEt) \cdot CHBr \cdot SEt + EtSH \longrightarrow (III)\ CH_3 \cdot C(SEt){:}CH(SEt) + HBr$$

* These structures are of much greater importance in the transition state, *i.e.*, when alkoxide ion is present, than in the ground state of the molecule.

The difficulty of adding ethylthiol to either of the unsaturated bis-sulphides (III) or (V) (experimental portion) eliminates the possibility that the tris-sulphide is formed from these substances, whereas it is to be expected that potassium carbonate would assist the first reaction and prevent the decomposition of the tris-sulphide once it was formed. The second reaction is in accord with the known instability of thioacetals to acids.

The formation of the two sulphones (I) and (II) as a result of oxidation may be due to two simultaneous decompositions. The preferential elimination of the β-ethylsulphonyl group from ααβ-tris(ethylsulphonyl)propane, $CH_3 \cdot CH(SO_2Et) \cdot CH(SO_2Et)_2$, would afford the αα-bis-sulphone (I) and the decomposition of the tris-sulphide by the acetic acid present in the oxidation mixture would lead to the production of the αβ-bis-sulphide (III), which would then furnish the αβ-bis-sulphone :

$$CH_3 \cdot CH(SEt) \cdot CH(SEt)_2 + HOAc \longrightarrow CH_3 \cdot CH(SEt) \cdot CH(OAc) \cdot SEt \longrightarrow (III) \longrightarrow (II).$$

EXPERIMENTAL.

Propaldehyde diethylacetal was conveniently prepared (yield, 50%) by allowing a mixture of propaldehyde (200 g.) and a 1% solution of hydrogen chloride in absolute ethyl alcohol (500 g.) to stand for 1 hour, diluting it with water (2—3 l.), and drying the separated acetal with fused calcium chloride. Its conversion into α-bromopropaldehyde diethylacetal was carried out by direct bromination (Burtles, Pyman, and Roylance, J., 1925, **127**, 585).

Condensation of α-Bromopropaldehyde Diethylacetal with Ethylthiol.—(i) Ethylthiol (84 c.c.) was slowly added to a stirred mixture of the bromo-acetal (106 g.), glacial acetic acid (200 c.c.), and 48% hydrobromic acid (200 c.c.) cooled in ice. After standing overnight, water was added, the product extracted with ether, and the extract washed with sodium bicarbonate solution and dried. Distillation yielded diethyl disulphide (15 g.) together with two fractions, b. p.'s 88—93°/9 mm. and 95—97°/9 mm., the yields being 3·5 g. and 19·0 g. respectively. These were essentially the same substances and, although they still contained traces of halogen, were mainly αβ-*bis(ethylthio)*-Δ^α-*propene* (III) (Found : C, 52·2; H, 8·9; S, 39·4. $C_7H_{14}S_2$ requires C, 51·9; H, 8·6; S, 39·5%). Oxidation furnished the corresponding bis-sulphone (II) described below.

(ii) The bromo-acetal (174 g.), ethylthiol (175 g.), and glacial acetic acid (500 c.c.) were mixed, cooled in a freezing mixture, and stirred while 40% hydrobromic acid (500 c.c.) was slowly added; the stirring was continued for a further 48 hours. After dilution the oil was extracted with xylene, and the extract washed with water, dried with fused calcium chloride, filtered, and refluxed for 6 hours with anhydrous potassium carbonate (80 g.). The xylene and other more volatile products (chiefly ethylthiol and diethyl disulphide) were removed by distillation in steam, and the residue extracted with ether. The ethereal solution yielded ααβ-*tris(ethylthio)propane* (IV), b. p. 100°/0·3 mm., 137—139°/9 mm.; yield, 72% (Found : C, 48·6; H, 8·7; S, 42·6. $C_9H_{20}S_3$ requires C, 48·2; H, 8·9; S, 42·9%).

Condensation of α-Bromopropaldehyde with Ethylthiol.—The aldehyde (30 g.), dissolved in carbon tetrachloride (30 c.c.), was cooled in a freezing mixture, and ethylthiol (40 c.c.) added. Dry hydrogen chloride was passed through the mixture for ¾ hour, and the liquid washed with water, dissolved in glacial acetic acid (300 c.c.), and oxidised with perhydrol (150 c.c.). The bulk of the product was an oil which after standing in a refrigerator deposited a mixture of αα- and αβ-bis(ethylsulphonyl)-Δ^α-propenes (I and II).

Oxidation of ααβ-Tris(ethylthio)propane.—The tris-sulphide (10 g.) in glacial acetic acid (150 c.c.) was oxidised with perhydrol (50 c.c.). When the very vigorous reaction had subsided, the liquid was heated for a further 10 minutes at 100°, and the sulphones extracted with chloroform. The crude solid was washed with ether, affording 7 g. of residue (26% yield). The ethereal washings were cooled and carefully treated with petrol (b. p. 40—60°), thereby yielding a *sulphone*, crystallising from ethyl acetate in needles having m. p. 114—115° and probably stereoisomeric with that (m. p. 73—74°) described below (Found : C, 37·1; H, 6·2; S, 28·3. $C_7H_{14}O_4S_2$ requires C, 37·2; H, 6·2; S, 28·3%).

The main bulk of the product was dissolved in hot methyl alcohol, which deposited αα-bis-(ethylsulphonyl)-Δ^α-propene (I) on cooling to room temperature. The sulphone separated from ethyl acetate in opaque cubic crystals, m. p. 95·3° [Found : C, 37·4; H, 6·4; S, 28·4; *M* (benzene),* 213, 233. Calc. : C, 37·2; H, 6·2; S, 28·3%; *M*, 226].

* The molecular weight found by Rast's method was usually very high, possibly owing to interaction with the camphor, and this was true of most of the sulphones described in this paper.
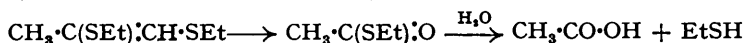
The methyl-alcoholic filtrate was evaporated to dryness, and the residue recrystallised from ether, from which αβ-*bis(ethylsulphonyl)*-Δ^α-*propene* (II) separated in transparent prisms, m. p. 73—74° (Found : C, 37·4; H, 6·1; S, 28·5; *M*, 219. $C_7H_{14}O_6S_2$ requires C, 37·2; H, 6·2; S, 28·3%; *M*, 226).

The amounts of the sulphones (I) and (II) were approximately equal; that of the first (m. p. 114—115°) was very much less and this sulphone was sometimes not isolated at all. About half the total oxidation product did not solidify, but on distillation three fractions were obtained, b. p. 135—143°/0·4 mm., 143—152°/0·4 mm., and 153—160°/0·4 mm. In each case partial crystallisation took place, the first two fractions affording the αα- and the · last the αβ-bis-sulphone. The serious loss during the oxidation of both the tris-sulphide and the bis-sulphide was probably due to decomposition by the acetic acid, since large quantities of ethylthiol were evolved when these compounds were boiled with the acid.

Oxidation of αβ-*Bis(ethylthio)*-Δ^α-*propene.*—The sulphide (3·5 g.) in glacial acetic acid (50 c.c.) was oxidised with perhydrol (18 c.c.); the product after isolation was a syrupy solid, which after washing with ether furnished the αβ-bis-sulphone. A very small amount of the αα-isomeride may have been present in the residues.

Action of Reagents on the αβ-*Bis-sulphide.*—(i) *Potassium* tert.-*butoxide.* The sulphide (5 g.) was boiled for 20 hours under reflux with 6% potassium *tert.*-butoxide (50 g.), washed with water and dried. Distillation yielded unchanged bis-sulphide, which oxidation converted into the corresponding sulphone in 40% yield.

(ii) *Fission by ozone.* A chloroform solution of the bis-sulphide (2 g.) was treated with ozonised oxygen for 20 hours, and the solvent removed in a vacuum at room temperature. The residue was shaken with water for 4 hours and extracted with ether. The extract yielded a *sulphide* (0·6 g.), b. p. 115—118°/9 mm. (Found : C, 33·3; H, 8·8; S, 40·3%), and the aqueous layer furnished, in addition to traces of acetaldehyde (identified by its 2 : 4-dinitrophenyl-hydrazone), acetic acid (0·21 g.), which was converted into the *p*-bromophenacyl ester, m. p. 85—87° (Found : C, 46·4; H, 3·6; Br, 31·2. Calc. : C, 46·7; H, 3·5; Br, 31·1%). The probable reaction is :
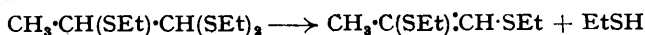
$$CH_3 \cdot C(SEt) \vcentcolon CH \cdot SEt \longrightarrow CH_3 \cdot C(SEt) \vcentcolon O \xrightarrow{H_2O} CH_3 \cdot CO \cdot OH + EtSH$$

Action of Reagents on ααβ-*Tris(ethylthio)propane.*—(i) *Sulphuric acid.* Complete decomposition and formation of diethyl disulphide.

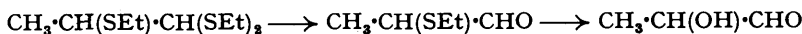(ii) *Methyl alcohol and sodium methoxide.* Neither the alcohol nor 2N-sodium methoxide solution has any action.

(iii) *Ethyl-alcoholic potash.* A mixture of the unchanged tris-sulphide and αα-bis(ethyl-thio)-Δ^α-propene was obtained when the former was refluxed for 12 hours with 8N-ethyl-alcoholic potash.

(iv) *Potassium* tert.-*butoxide.* The tris-sulphide (9·9 g.) was refluxed for 4 hours with 1·54N-potassium *tert.*-butoxide (25 c.c.). The chief product was αα-bis(ethylthio)-Δ^α-propene (69%), which on oxidation afforded a 25% yield of the corresponding sulphone. No trace of the αβ-sulphone was detected. A smaller fraction (20%), b. p. 139—140°/9 mm., was probably the unchanged starting material, although only the αβ-sulphone was actually found when it was oxidised.

(v) *Mercuric oxide.* The tris-sulphide (4·0 g.) was refluxed for 3 hours with mercuric oxide (11 g.) and water (50 c.c.), and the product distilled in steam. The αβ-bis-sulphide (1·0 g.) was found in the distillate together with diethyl disulphide (0·8 g.) and acetaldehyde (2 : 4-dinitrophenylhydrazone. Found : C, 43·1; H, 3·6; N, 24·7. Calc. : C, 42·9; H, 3·6; N, 25·0%). The probable reaction was :

$$CH_3 \cdot CH(SEt) \cdot CH(SEt)_2 \longrightarrow CH_3 \cdot C(SEt) \vcentcolon CH \cdot SEt + EtSH$$

(vi) *Mercuric chloride.*

$$CH_3 \cdot CH(SEt) \cdot CH(SEt)_2 \longrightarrow CH_3 \cdot CH(SEt) \cdot CHO \longrightarrow CH_3 \cdot CH(OH) \cdot CHO$$

ααβ-Tris(ethylthio)propane (7·6 g.) was refluxed with mercuric chloride (150 g.), cadmium carbonate (10 g.), and water (100 c.c.). The precipitated ethylthiomercuric chloride and unchanged cadmium carbonate were filtered off, and the filtrate distilled in steam. Treatment of the steam-distillate with excess of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid afforded a precipitate partly soluble in hot ethyl alcohol, the residue consisting of the bright red methylglyoxal 2 : 4-dinitrophenylosazone, which separated from phenetole in needles, m. p. 295° (decomp.) (Found : C, 42·1; H, 3·3; N, 25·2. Calc. : C, 41·7; H, 2·8; N, 25·9%),

and was slightly contaminated with sulphur which was not easily eliminated. A sample of the osazone prepared from acetol and crystallised from phenetole was identical in appearance and also had m. p. 295° (decomp.); Ingold, Pritchard, and Smith (J., 1934, 79), crystallising it from acetic anhydride, found m. p. 299—300° (decomp.). The isomeric *malonaldehydebis-2 : 4-dinitrophenylhydrazone*, which was prepared from β-ethoxyacraldehyde diethylacetal, EtO·CH:CH·CH·(OEt)$_2$ (Claisen, *Ber.*, 1903, **36**, 3668), was quite different in appearance and crystalline form and was deposited from phenetole in microscopic clusters, m. p. 284° (decomp.) (Found : C, 41·5; H, 3·2; N, 25·2. C$_{15}$H$_{12}$O$_8$N$_8$ requires C, 41·7; H, 2·8; N, 25·9%).

The hot alcoholic solution deposited α-*ethylthiopropaldehyde-2 : 4-dinitrophenylhydrazone*, CH$_3$·CH(SEt)·CH:N·NH·C$_6$H$_3$(NO$_2$)$_2$, which after two recrystallisations from petrol (b. p. 80—100°) containing a trace of benzene separated in orange-red prisms, m. p. 95—96°, identical (m. p. and mixed m. p.) with the synthetic specimen described below (Found : C, 44·7; H, 4·8; N, 18·7; S, 11·0. C$_{11}$H$_{14}$O$_4$N$_4$S requires C, 44·3; H, 4·7; N, 18·8; S, 10·7%). Neither α-hydroxypropaldehyde nor methylglyoxal is formed when acraldehyde is boiled with aqueous mercuric chloride, and the aldehyde is recovered unchanged.

β-*Ethylthiopropaldehyde diethylacetal*, SEt·CH$_2$·CH$_2$·CH(OEt)$_2$, was prepared by boiling a mixture of β-chloropropaldehyde diethylacetal (17 g.), sodium ethylthiol (from 10 g. of ethylthiol), and ethyl alcohol (40 c.c.) for ½ hour. B. p. 94—97°/9 mm.; yield, 82% (Found : C, 56·0; H, 10·6; S, 16·5. C$_9$H$_{20}$O$_2$S requires C, 56·3; H, 10·4; S, 16·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in long, flat, yellow prisms, m. p. 107° (Found : C, 45·0; H, 4·6; S, 10·2. C$_{11}$H$_{14}$O$_4$N$_4$S requires C, 44·3; H, 4·7; S, 10·7%).

αγ-*Tris(ethylthio)propane*, SEt·CH$_2$·CH$_2$·CH(SEt)$_2$, was obtained in 96% yield by shaking a mixture of the above ethylthiopropaldehyde acetal (10 g.), ethylthiol (9 c.c.), glacial acetic acid (22 c.c.), and concentrated hydrochloric acid (22 c.c.); b. p. 87°/0·2 mm. (Found : C, 48·7; H, 8·7; S, 43·0. C$_9$H$_{20}$S$_3$ requires C, 48·2; H, 8·9; S, 42·9%). Oxidation with perhydrol furnished an 83% yield of αγ-*tris(ethylsulphonyl)propane*, crystallising from ethyl acetate in prisms, m. p. 105—106° (Found : C, 34·0; H, 6·1. C$_9$H$_{20}$O$_6$S$_3$ requires C, 33·8; H, 6·3%). No loss of ethylthiol was observed during the oxidation and the tris-sulphide was recovered unchanged when boiled with potassium *tert.*-butoxide.

Preparation of α-Ethylthiopropaldehyde and its Acetal.—Owing to the unreactivity of the halogen atom in the starting materials neither of these substances could be obtained pure.

α-*Ethylthiopropaldehyde diethylacetal*, CH$_3$·CH(SEt)·CH(OEt)$_2$, was obtained from α-bromopropaldehyde diethylacetal (15·3 g.), sodium ethylthiol (from 7 g. of ethylthiol), and alcohol (20 c.c.); b. p. 78—80°/9 mm.; yield, 3·5 g. Although the mixture was refluxed for 15 hours, the product still contained halogen, and it was not possible to separate the sulphur compound from the bromo-acetal (Found : C, 52·7; H, 9·6; S, 12·7. C$_9$H$_{20}$O$_2$S requires C, 56·3; H, 10·4; S, 16·7%). The 2 : 4-dinitrophenylhydrazone obtained therefrom, however, was identical with that previously prepared (Found : C, 44·8; H, 4·8%).

The above reaction having proved unsatisfactory, α-bromopropaldehyde was used as a starting material and in this case there was an immediate precipitation of sodium bromide when the aldehyde (14 g.) was mixed with an alcoholic solution of sodium ethylthiol (from 8 g. of ethylthiol). Here again, however, the α-*ethylthiopropaldehyde* (b. p. 34—37°/9 mm.; yield, 41%) was impure and the substance contained too much sulphur (Found : C, 48·5; H, 8·5; S, 28·5. C$_5$H$_{10}$OS requires C, 50·8; H, 8·5; S, 27·1%), but the same 2 : 4-dinitrophenylhydrazone was obtained.

ααβ-Tris(ethylthio)propane was prepared from α-ethylthiopropaldehyde (5 g.) dissolved in 80% acetic acid (5 c.c.), to which was added with shaking first ethylthiol (6 c.c.) and then concentrated hydrochloric acid (10 c.c.). Yield, 64% (Found : C, 48·5; H, 9·0; S, 42·9%). Oxidation of this compound afforded a mixture of αα- and αβ-bis(ethylsulphonyl)-Δ^α-propene as in previous cases.

A mixture of ααβ-tris(ethylthio)propane (2·8 g.) and 5% potassium *tert.*-butoxide was refluxed, and the solution acidified with dilute sulphuric acid, the liberated ethylthiol being passed through a solution of mercuric cyanide by means of a current of nitrogen. The precipitated mercury bis-ethylthiol was identified by comparison with an authentic specimen (m. p. and mixed m. p.). Some diethyl disulphide was obtained from the acidified liquid (formed by the decomposition of the bis-sulphide by the acid), the bulk of the product being αα-bis(ethylthio)-Δ^α-propene.

α-n-*Butylthiopropaldehyde*, CH$_3$·CH(SBu)·CHO, was prepared from butylthiol (16 g.), sodium ethoxide (4·6 g. of sodium in 100 c.c. of alcohol), and freshly distilled α-bromopropaldehyde, the mixture being stirred for 3 hours; b. p. 71·5—72·5°/9 mm.; yield, 51% (Found :

C, 57·5; H, 9·9; S, 22·0. $C_7H_{14}OS$ requires C, 57·5; H, 9·6; S, 21·9%). The 2 : 4-*dinitro-phenylhydrazone* crystallised from ethyl alcohol in orange-red needles, m. p. 107—109° (Found : C, 48·1; H, 5·8; S, 9·0. $C_{13}H_{18}O_4N_4S$ requires C, 47·9; H, 5·5; S, 9·8%).

When the above aldehyde (10 g.), mixed with ethylthiol (16 c.c.) and 80% acetic acid (10 c.c.), was shaken with hydrochloric acid (10 c.c.), there resulted αα-*bis*(*ethylthio*)-β-n-*butyl-thiopropane* (VI), b. p. 114—116°/0·3 mm.; yield, 46·5% (Found : C, 52·4; H, 9·4; S, 37·9. $C_{11}H_{24}S_3$ requires C, 52·4; H, 9·5; S, 38·0%). In addition there was also a fraction, b. p. 105—110°/0·3 mm. (yield, 25·5%), this being substantially the same substance.

Oxidation. This was accomplished in the usual way with perhydrol. A mixture of a solid and an oil was obtained, which were separated by washing with ether, the residue being αα-bis(ethylsulphonyl)-Δ^α-propene (Found : C, 37·4; H, 6·2%). The ether was distilled off from the syrupy portion, which crystallised after standing for a day in the refrigerator. The solid was α-*ethylsulphonyl*-β-n-*butylsulphonyl*-Δ^α-*propene* (VII), which crystallised from ether in needles, m. p. 52° (Found : C, 42·5; H, 7·2; S, 25·3. $C_9H_{18}O_4S_2$ requires C, 42·5; H, 7·1; S, 25·2%).

αα-Bis(ethylthio)-β-n-butylthiopropane (5·5 g.) was boiled for 6 hours with 6% potassium *tert.*-butoxide solution (100 g.). The liquid was shaken with water, and the aqueous layer extracted with ether, which was then added to the butyl alcohol, and the latter dried with anhydrous potassium carbonate and fractionated. αα-Bis(ethylsulphonyl)-Δ^α-propene was obtained by the oxidation of the sulphide (yield of sulphide, 2·4 g., together with 0·8 g. of higher-boiling substance) and no ethylsulphonyl-n-butylsulphonylpropene was detected. The aqueous layer from the ethereal extraction was acidified with dilute sulphuric acid, affording n-butylthiol, identified (m. p. and mixed m. p. with a synthetic specimen) as *mercury bisbutyl-thiol* (Found : C, 24·7; H, 4·7. $C_8H_{18}S_2Hg$ requires C, 25·4; H, 4·7%).

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