295. *Oxidation of Organic Sulphides. Part VIII.*[1] *Autoxidation of Thiacyclohexane, 2-Ethyl-2-methyl-5-*iso*propylthiacyclopentane, and Thiacyclohex-3-ene.*

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The above-named cyclic sulphides react with oxygen by mechanisms similar to those advanced previously for their respective acyclic analogues. A practical point of difference is that in reactions involving rupture of C–S bonds, the products produced in the latter systems are replaced in the former by " dimeric " products arising from ring opening and subsequent combination of RS• radicals.

IN Parts IV [2] and VII [1] the reaction of oxygen with certain saturated and unsaturated acyclic sulphides was described, and reaction mechanisms were postulated which were consistent both with the complex product and kinetic data and with independent information on hydroperoxide–sulphide interactions.[3] These studies have now been extended to cyclic sulphides, since these structures occur in ordinary vulcanized rubber [4] whose autoxidation is of great technological importance.

Inert by itself, thia*cyclo*hexane reacts readily with oxygen at moderate temperatures in the presence of catalytic amounts of azo*iso*butyronitrile to produce water and sulphoxide groups in yields which vary little with the extent of reaction—features previously found to be characteristic of saturated acyclic sulphides.[1] The sulphoxide groups are located wholely in thia*cyclo*hexane oxide, and the other main reaction product is the dialdehydic disulphide (I), which was characterized by the formation of a bis-2 : 4-dinitrophenylhydrazone, and by reduction to 5-mercaptopentan-1-ol on treatment with lithium aluminium hydride.

The disulphide (I) has no parallel in the oxidation products of acyclic sulphides, but its formation is readily explained by a series of reactions analogous to that postulated for *n*-butyl methyl sulphide,[1] with the logical difference that the derived α-thio-oxy-radicals undergo scission at the C–S bond to open the thia*cyclo*hexane ring and to liberate SMe groups respectively (see scheme).

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\begin{array}{lrcll}
\text{Free-radical chain initiation:} & \text{RH} & \xrightarrow{-\text{H}} & \text{R}\cdot & \quad (1)\\
\text{Chain propagation:} & \text{R}\cdot + \text{O}_2 & \longrightarrow & \text{R}\cdot\text{O}_2\cdot & \quad (2)\\
 & \text{R}\cdot\text{O}_2\cdot + \text{RH} & \longrightarrow & \text{R}\cdot\text{O}_2\text{H} + \text{R}\cdot & \quad (3)\\
\text{Sulphoxide formation:} & \text{R}\cdot\text{O}_2\text{H} + \text{RH} & \longrightarrow & \text{R}\cdot\text{OH} + \text{Sulphoxide} & \quad (4)\\
\left.\begin{array}{l}\\ \text{Decomp. of monothioacetal and}\\ \quad\text{hydroperoxide:}\\ \\ \end{array}\right\} & \left\{\begin{array}{r}\text{R}\cdot\text{OH}\\ \text{R}\cdot\text{O}_2\text{H}\\ \\ \text{HO}\cdot + \text{RH}\end{array}\right. & \begin{array}{c}\longrightarrow\\ \longrightarrow\\ \longleftrightarrow\\ \longrightarrow\end{array} & \begin{array}{l}\text{H}_2\text{O} + \text{Polymers}\\ \text{HO}\cdot + \text{R}\cdot\text{O}\cdot\\ \cdot\text{S}\cdot[\text{CH}_2]_4\cdot\text{CHO} \longrightarrow \tfrac{1}{2}(\text{I})\\ \text{H}_2\text{O} + \text{R}\cdot\end{array} & \begin{array}{l}\quad (5)\\ \\ \quad (6)\\ \quad (7)\end{array}\\
 & & & (\text{R} = \text{thia}\textit{cyclo}\text{hex-2-yl}) &
\end{array}
$$

If it is assumed that two-thirds of the hydroperoxide formed in reaction (3) participates in reaction (4) and the remainder in reaction (6), the relative yields of sulphoxide, water, and disulphide (I) are 1·0 : 1·5 : 0·25, which is essentially the experimental finding, *viz.*, 1·0 : 1·3 : 0·2, with 95% of the absorbed oxygen accounted for.

The autoxidation of 2-ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane (a product of the reaction of sulphur with the di-isoprenic, 2 : 6-dimethylocta-2 : 6-diene) [4] follows a pattern similar to the above. Sulphoxide, water, and a " dimeric " derivative are again the principal products, but in this case the last is not simply the analogue of (I), *i.e.*, (II),

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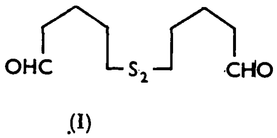
[1] Part VII, Bateman, Cunneen, and Ford, *J.*, 1956, 3056.

[2] Bateman and Shipley, *J.*, 1955, 1996.

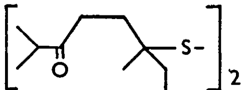
[3] Bateman and Hargrave, *Proc. Roy. Soc.*, 1954, *A*, **224**, 389, 399; Hargrave *ibid.*, 1956, *A*, **235**, 55.

[4] Bateman, Glazebrook, Moore, and Saville, Proc. Third Internat. Rubber Tech. Conf., London, 1954, p. 298.

but also comprises in major amount the monoketone (III). The monoketone could be separated from the diketone (II) by vacuum-distillation, and was characterized by elemental



(I)



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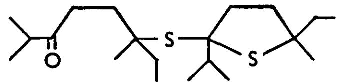
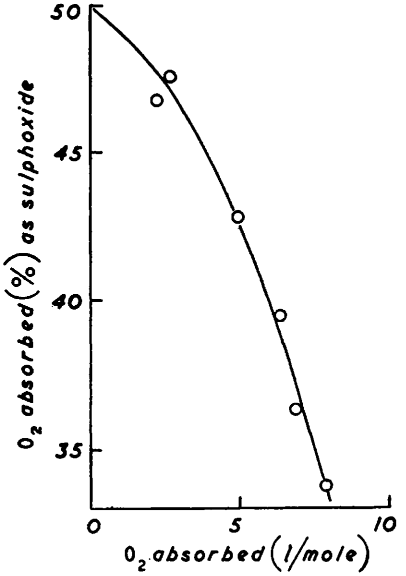


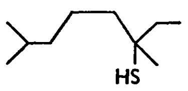
(III)

analysis, molecular weight, infrared absorption at 1720 cm.$^{-1}$ (associated with a saturated carbonyl group), formation of a liquid mono-2 : 4-dinitrophenylhydrazone, and reduction to the thiols (IV) and (V) and the original sulphide on treatment by lithium aluminium hydride (reflecting selective response of thioacetal-type C–S bonds to this reagent).

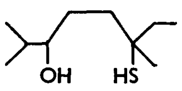


Variation in yield of sulphoxide during autoxidation of thiacyclohex-3-ene at 55°.

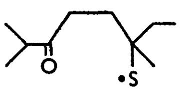
The formation of the monoketone (III) in preference to that of the diketone (II) appears indicative of favoured cross-termination of the radicals (VI) and (VII) rather than mutual combination of (VI) as in reaction (6). This is in keeping with the trend observed with highly reactive and heavily substituted olefinic systems.[5] If one adopts the reaction



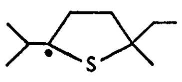
(IV)



(V)



(VI)



(VII)

scheme given above, with one-quarter of the hydroperoxide produced as in reaction (3) participating in reaction (4) and the remainder in reaction (6), and with five out of seven radicals (VI) produced as in (6) combining with (VII), the relative yields of sulphoxide, water, and products (II) and (III) are 1·0 : 4·0 : 0·5 : 2·1 compared with the experimentally observed 1·0 : 3·3 : 0·4 : 2·4, and 82% of the absorbed oxygen is thus accounted for.

The unsaturated cyclic sulphide, thia*cyclo*hex-3-ene, readily reacted with oxygen in the absence of catalyst and, simulating further the acyclic analogues,[1] the sulphoxide was formed in approximately 50% yield (based on the oxygen absorbed) at the beginning of the reaction which fell markedly as reaction proceeded (Figure). The products consisted of thia*cyclo*hex-3-ene oxide, water, and a sulphur-containing aldehyde mixture. After separation by chromatography over silica gel, the last polymerized fairly readily at room

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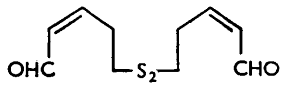
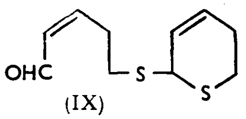
[5] Bateman and Morris, *Trans. Faraday Soc.*, 1953, **49**, 1026.

temperature, but if distilled rapidly in a vacuum immediately after isolation yielded a compound $C_{10}H_{14}OS_2$ identified as the monoaldehyde (IX) by its spectroscopic properties and by formation of a crystalline 2 : 4-dinitrophenylhydrazone. Treatment of the mixture before distillation with Brady's reagent gave a solid heterogeneous 2 : 4-dinitrophenylhydrazone, whose analysis showed it to be derived mainly from a product containing one aldehyde group associated with each sulphur atom as well as from (IX). By this fact, the formation of the product (IX), and analogy with the oxidative fission of saturated cyclic sulphides as described above, this product is almost certainly the dialdehyde (VIII). There can be little doubt, therefore, that the autoxidation proceeds by the variant of the reaction scheme previously advanced for unsaturated sulphides, *i.e.*, by reactions identical with (1)—(4) and then the sulphoxide participates self-destructively in the subsequent decompositions.[1, 3]



(VIII)



(IX)

EXPERIMENTAL

Thia*cyclo*hexane, prepared from 1 : 5-dibromopentane and hydrated sodium sulphide,[6] had b. p. 140—141°/760 mm., n_D^{20} 1·5062 (Found : C, 58·8; H, 9·8; S, 31·55. Calc. for $C_5H_{10}S$: C, 58·9; H, 9·8; S, 31·4%). The derived sulphoxide had b. p. 127—128°/15 mm., n_D^{35} 1·5080 (Found : SO content, 98·0%), and the sulphone [6] had m. p. 97—98° after crystallisation from ethanol.

2-Ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane [7] had b. p. 86·5°/12 mm., n_D^{20} 1·4765 (Found : C, 70·05; H, 11·4; S, 18·6. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%). The *sulphoxide* had b. p. 72—74°/0·01 mm., n_D^{20} 1·4892 (Found : C, 64·0; H, 10·55; S, 16·6; SO content 98·4. $C_{10}H_{20}OS$ requires C, 63·8; H, 10·6; S, 17·0%).

*Synthesis of Thia*cyclo*hex-3-ene.*—Thia*cyclo*hexan-4-ol (53 g.), m. p. 52—53°, was obtained by reduction of thia*cyclo*hexan-4-one [8] (62 g.) with lithium aluminium hydride (10 g.) in dry ether (500 ml.). Dehydration of the alcohol (40 g.) with boric acid (20 g.), first at 190° and later at 300°, gave thia*cyclo*hex-3-ene (20 g.), b. p. 71—72°/60 mm., n_D^{20} 1·5346 (Found : C, 59·85; H, 8·0; S, 32·0. Calc. for C_5H_8S : C, 60·0; H, 8·0; S, 32·0%). The derived *sulphoxide* had b. p. 71·5°/0·002 mm., n_D^{20} 1·5483 (Found : C, 51·2; H, 6·9; S, 27·1; SO content, 98·2. C_5H_8OS requires C, 51·75; H, 6·9; S, 27·6%). The sulphone had m. p. 72° (Found : C, 45·2; H, 6·1; S, 24·2. Calc. for $C_5H_8O_2S$: C, 45·4; H, 6·1; S, 24·2%).

Oxidations.—Oxidations were carried out in the apparatus described in Part VII.[1] The saturated sulphides were oxidised at 75° in the presence of $\alpha\alpha'$-azo*iso*butyronitrile (1%); thia*cyclo*hex-3-ene was oxidised at 55° without catalyst.

*Separation and Identification of the Oxidation Products of Thia*cyclo*hexane.*—The oxidised sulphide (65·37 g. containing 0·94 g. of oxygen) was heated at 50° (bath)/11 mm. and the volatile materials (59·7 g.) were collected at −80°. The infrared spectrum of the volatile product after drying (Found : C, 58·95; H, 9·75; S, 31·5%) was identical with that of the original sulphide. The involatile residue (A) (5·6 g.) had n_D^{20} 1·5040 (Found : C, 52·7; H, 8·55; N, 1·9; S, 23·0; SO content, 51%; *M*, 210); strong absorption at 1720 cm.$^{-1}$ indicated the presence of saturated carbonyl groups, and Schiff's reagent showed the presence of aldehyde groups.

A solution of the residue (A) (8·15 g.) in tetrahydrofuran was added to excess of lithium aluminium hydride in the same solvent and refluxed for 2 hr. Working up in the usual way followed by fractional distillation gave : (i) thia*cyclo*hexane (4 g.), b. p. 63—64°/50 mm., n_D^{20} 1·5052, infrared spectrum identical with that of the pure sulphide; (ii) (1·3 g.), b. p. 101°/10 mm., n_D^{20} 1·4875 (Found : C, 49·7; H, 10·0; S, 26·75; SH content, 26·25. $C_5H_{12}OS$ requires C, 50·0; H, 10·0; S, 26·66; SH content, 27·5%), identified as 5-*mercaptopentan*-1-*ol* (see below). The derivative obtained on reaction with 1-chloro-2 : 4-dinitrobenzene had m. p. and mixed m. p. 95°.

Synthesis of 5-*Mercaptopentan*-1-*ol.*—Reduction of but-3-enoic acid (20 g.) with lithium

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[6] Whitehead, Dean, and Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3632.

[7] Glazebrook and Saville, *J.*, 1954, 2099.

[8] Fennel and Carmack, *J. Amer. Chem. Soc.*, 1948, **70**, 1813.

aluminium hydride gave pent-4-en-1-ol (10 g.), b. p. 140—142°/760 mm., n_{D}^{20} 1·4295, which reacted exothermally with thioacetic acid (9 g.) to give 5-*acetylthiopentan*-1-*ol* (12 g.), n_{D}^{20} 1·4889 (Found: C, 52·0; H, 8·75; S, 19·6. $C_7H_{14}O_2S$ requires C, 51·9; H, 8·65; S, 19·75%). Alkaline hydrolysis of this ester gave 5-mercaptopentan-1-ol (8 g.), b. p. 104°/11 mm., n_{D}^{20} 1·4865 (Found: C, 49·8; H, 10·05; S, 26·4; SH content, 28·0%), which gave the 2 : 4-*dinitrophenyl sulphide*, yellow plates (from ethanol), m. p. 95° (Found: C, 46·15; H, 4·85; N, 9·8. $C_{11}H_{14}O_5N_2S$ requires C, 46·1; H, 4·82; N, 9·78%).

Reaction of Residue (A) *with* 2 : 4-*Dinitrophenylhydrazine*.—Residue (A) (4 g.) was treated with excess of 2 : 4-dinitrophenylhydrazine hydrochloride in ethanol, water added until no further precipitation occurred, and the mixture kept for 48 hr. at room temperature. The solid was filtered off, washed thoroughly with 2N-hydrochloric acid, and then with water, dried, dissolved in benzene, and poured on a column of alumina. Elution with 1 : 1 benzene–ethyl acetate, followed by evaporation, gave the 2 : 4-dinitrophenylhydrazone of the aldehydic *disulphide* (I) (1·45 g.), m. p. 122·5—124° (from benzene–*cyclo*hexane) (Found: C, 44·45; H, 4·65; N, 18·7; S, 10·75%; *M*, 640. $C_{22}H_{26}O_8N_8S_2$ requires C, 44·4; H, 4·4; N, 18·8; S, 10·8%; *M*, 594).

Separation of Residue (A) *by Counter-current Distribution*.—Residue (A) (5 g.) was partitioned between water and ether in an apparatus containing 25 cells. The water layers were saturated with salt and extracted with chloroform which on evaporation gave thia*cyclo*hexane oxide (1·2 g.), b. p. 60—62°/0·001 mm. (Found: SO content, 98·4%). Oxidation with acid permanganate gave the corresponding sulphone, m. p. and mixed m. p. 97—98°. The ether layers, on evaporation, gave an oil (1·9 g.) which rapidly polymerised to a rubber-like material.

*Oxidation of Thia*cyclo*hexane in the Presence of the Sulphoxide*.—The sulphide (9·83 g.) containing thia*cyclo*hexane oxide (0·494 g.) and αα′-azo*iso*butyronitrile (0·095 g.) was shaken in oxygen at 75° until 1·45 wt.-% had been absorbed. The sulphoxide content was then 8·3%; the calculated value on the basis that the added sulphoxide behaves as a neutral diluent having no influence on the oxidation is 8·2% (cf. *n*-butyl methyl sulphide).

Separation and Identification of the Oxidation Products of 2-*Ethyl*-2-*methyl*-5-iso*propylthia*cyclo*pentane*.—Distillation of the oxidised sulphide (74 g. containing 1·27 g. of oxygen) at 50° (bath)/0·01 mm. gave a volatile fraction (60 g.) which contained water. After drying, infrared examination showed this fraction to be identical with the original sulphide (Found: C, 70·0; H, 11·3; S, 18·4%). The involatile residue (B) (13·83 g.) had n_{D}^{20} 1·5008 (Found: C, 65·7; H, 10·6; N, 0·5; S, 17·5; SO content, 10·0%). Schiff's reagent indicated the absence of aldehyde groups, but strong infrared absorption at 1720 cm.$^{-1}$ showed the presence of saturated carbonyl groups.

Residue (B) (10 g.) was partitioned between light petroleum (b. p. <40°) and water in the usual way, the water layers yielding a product which on distillation gave 2-ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane oxide (1·03 g.), b. p. 73—75°/0·01 mm., n_{D}^{20} 1·4900 (Found: C, 64·2; H, 10·2; S, 17·1; SO content, 95·4%). The corresponding sulphone [7] had b. p. 79°/0·002 mm., n_{D}^{20} 1·4777. Evaporation of the light petroleum gave a mixture of ketones (C) (8·55 g.), (Found: C, 66·0; H, 10·45; N, 0·2; S, 17·55; SO content, 0·0%; *M*, 390. Calc. for 80% of $C_{20}H_{38}OS_2$ and 20% of $C_{20}H_{38}O_2S_2$: C, 66·35; H, 10·5; S, 17·7%; *M*, 350).

Mixture (C) (2·0 g.) with Brady's reagent gave a liquid derivative (2·34 g.) (Found: C, 56·6; H, 7·75; N, 11·55; S, 11·1%; *M*, 640. Calc. for 80% of $C_{26}H_{42}O_4N_4S_2$ and 20% of $C_{32}H_{46}O_8N_8S_2$: C, 56·9; H, 7·5; N, 11·4; S, 11·2%; *M*, 576). A portion of this derivative (1·1 g.) in carbon tetrachloride (200 ml.) was passed down a column (2 × 20 cm.) of alumina followed by (1) carbon tetrachloride (200 ml.) and (2) 1 : 4 carbon tetrachloride–benzene (100 ml.). When worked up, fraction (1) gave the 2 : 4-*dinitrophenylhydrazone* (0·89 g.) (Found: C, 58·15; H, 7·85; S, 11·75%; *M*, 525. $C_{26}H_{42}O_4N_4S_2$ requires C, 58·0; H, 7·8; S, 11·8%; *M*, 538) of the ketone (III), and fraction (2) gave the 2 : 4-*dinitrophenylhydrazone* (0·2 g.) (Found: C, 52·4; H, 6·25; S, 8·8. $C_{32}H_{46}O_8N_8S_2$ requires C, 52·3; H, 6·2; S, 8·7%) of the keto-disulphide (II); both products were liquids.

Reduction of the ketone (III) *with lithium aluminium hydride*. Distillation of the mixture (C) (20 g.) gave (i) a forerun (1·0 g.), b. p. >144°/0·001 mm., n_{D}^{20} 1·5000, and (ii) 2-*ethyl*-5-(1-*ethyl*-1 : 5-*dimethyl*-4-*oxohexylthio*)-2-*methyl*-5-iso*propylthia*cyclo*pentane* (III) (13 g.), b. p. 144—145°/0·001 mm., n_{D}^{20} 1·5010 (Found: C, 66·8; H, 10·4; S, 17·8%; *M*, 360. $C_{20}H_{38}OS_2$ requires C, 67·1; H, 10·6; S, 17·9%; *M*, 358); the intensity of the infrared absorption at 1720 cm.$^{-1}$ was indicative of the purity of this product.

Reduction of the ketone (III) (10 g.) with lithium aluminium hydride (3 g.) in dry tetrahydrofuran (40 ml.), and isolation of the product gave a liquid (9·2 g.), which on fractional distillation yielded: (i) a mixture of the original sulphide and 2 : 6-dimethyloctane-6-thiol (IV) (4·15 g.), b. p. 85—88°/11 mm., n_{D}^{20} 1·4760 (Found: C, 69·3; H, 11·75; S, 18·35; SH, 9·3%; *M*, 170. Calc. for 52% of $C_{10}H_{20}S$ and 48% of $C_{10}H_{22}S$: C, 69·25; H, 12·25; S, 18·5; SH, 9·3%; *M*, 172); infrared analysis confirmed that this mixture contained ~50% of the original sulphide; (ii) 6-*mercapto*-2 : 6-*dimethyloctan*-3-*ol* (V) (3·5 g.), b. p. 63—64°/0·002 mm., n_{D}^{20} 1·4790 (Found: C, 63·1; H, 11·6; S, 16·75; SH, 17·6%; *M*, 186. $C_{10}H_{22}OS$ requires C, 63·25; H, 11·6; S, 16·8; SH, 17·4%; *M*, 190).

Fraction (i) (4·0 g.) in ethanol (25 ml.) was refluxed with sodium (0·5 g.) in ethanol (25 ml.) for 10 min. After evaporation the solid residue (1·2 g.) was washed with light petroleum (b. p. <40°), and the distillate and the washings were poured into excess of water and extracted four times with light petroleum. Evaporation of the light petroleum gave the original sulphide (1·75 g.), b. p. 85—86°/11 mm., n_{D}^{20} 1·4760, identified by infrared examination. The solid residue (1·2 g.) was dissolved in water and acidified and then extracted with light petroleum. Distillation of the residue obtained after evaporation of the light petroleum gave 2 : 6-*dimethyloctane*-6-*thiol* (IV) (0·6 g.), b. p. 89°/10 mm., n_{D}^{20} 1·4760 (Found: C, 69·2; H, 12·2; S, 17·95; SH, 17·6. $C_{10}H_{22}S$ requires C, 69·0; H, 12·6; S, 18·3; SH, 18·95%).

Reduction of the ketonic mixture (C) *with lithium aluminium hydride.* The mixture (C) (7·8 g.) was treated with lithium aluminium hydride, and the product isolated in the usual way. The liquid (7·3 g.) obtained gave on distillation: (i) a mixture of the original sulphide and 2 : 6-dimethyloctane-6-thiol (IV) (2·78 g.), b. p. 85—89°/11 mm., n_{D}^{20} 1·4760 (Found: SH, 9·3%); (ii) 6-mercapto-2 : 6-dimethyloctan-3-ol (V) (3·0 g.), b. p. 63—64°/0·002 mm., n_{D}^{20} 1·4792 (Found: C, 63·95; H, 11·55; S, 17·0; SH, 16·5%; *M*, 186).

Oxidation of 2-*Ethyl*-2-*methyl*-5-iso*propylthia*-cyclo*pentane in the Presence of the Sulphoxide.*—The sulphide (8·78 g.) containing 2-ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane oxide (0·211 g.) and αα′-azo*iso*butyronitrile (0·089 g.) was shaken in oxygen until 1·65 wt.-% was absorbed. The sulphoxide content was then 4·0%; the calculated value on the basis that the added sulphoxide behaves as a neutral diluent having no influence on the oxidation is 4·4%.

*Separation and Identification of the Oxidation Products of Thia*cyclo*hex*-3-*ene.*—The oxidised sulphide (44·31 g. containing 1·56 g. of oxygen) was distilled at 50° (bath)/11 mm.; a volatile fraction (33·6 g.) which contained water was obtained and an involatile residue (D) remained. Infrared examination of the volatile fraction after drying indicated that it was unchanged sulphide (Found: C, 59·75; H, 8·1; S, 31·95%). The residue (D) (10·5 g.) had n_{D}^{20} 1·5580 (Found: C, 52·6; H, 8·7; S, 27·45; SO, 50·0%; *M*, 150); infrared analysis in carbon tetrachloride indicated the presence of the following functional groups: SO (1044 cm.$^{-1}$), C:C·CO (1700 cm.$^{-1}$), C:C·S (1598 cm.$^{-1}$), and OH (3602 cm.$^{-1}$). Reaction with Schiff's reagent indicated the presence of aldehyde groups.

Residue (D) (7·3 g.) in carbon tetrachloride (200 ml.) was passed down a column (50 × 2·0 cm.) of silica gel (200-mesh) followed by (1) 3 : 1 carbon tetrachloride–ether (200 ml.), (2) ether (200 ml.), and (3) methanol (300 ml.). On working up these fractious, (1) gave a liquid (E) (3·1 g.), n_{D}^{20} 1·5980 (Found: C, 53·8; H, 6·85; S, 27·9; SO, 5·0%; *M*, 187), which polymerised at room temperature, with 2 : 4-dinitrophenylhydrazine in ethanol gave a heterogeneous hydrazone, m. p. 110—118° (Found C, 45·95; H, 4·4; S, 12·65%; *M*, 510. Calc. for 32% of $C_{16}H_{18}O_4N_4S_2$ and 68% of $C_{22}H_{22}O_8N_8S_2$: C, 46·0; H, 4·0; S, 12·55%; *M*, 528), and on evaporative distillation immediately after isolation gave 5-(*thia*cyclo*hex*-3-*en*-2-*ylthio*)-*pent*-2-*enal* (IX), b. p. 50°/0·001 mm., n_{D}^{20} 1·5954 (Found: C, 56·4; H, 6·5; S, 29·8; SO, 0%; *M*, 220. $C_{10}H_{14}OS_2$ requires C, 56·1; H, 6·5; S, 29·9%; *M*, 214), infrared bands at 1700 (C:C·CO) and 1598 cm.$^{-1}$ (C:C·S), which with Brady's reagent gave the dark red 2 : 4-*dinitrophenylhydrazone*, m. p. 122° (from 1 : 1 benzene–*cyclo*hexane) (Found: C, 48·9; H, 4·6; N, 14·35%; *M*, 425. $C_{16}H_{18}O_4N_4S_2$ requires C, 48·7; H, 4·6; N, 14·2%; *M*, 394) [light absorption max. in EtOH at 3740 Å (ε 29,700)], of (IX). Fraction (2) gave only a trace of extract, but fraction (3) gave a product (3·5 g.) which on distillation yielded thia*cyclo*hex-3-ene oxide, b. p. 71—73°/0·002 mm., n_{D}^{20} 1·5480 (sulphone, m. p. and mixed m. p. 72°).

Residue (D) (3·0 g.) with lithium aluminium hydride in tetrahydrofuran gave thia*cyclo*hex-3-ene (1·75 g.), b. p. 70—72°/60 mm., n_{D}^{20} 1·5340, and a residue (0·85 g.), which contained thiol groups (lead acetate).

Quantitative Estimation of Oxidation Products.—*Sulphoxide and water.* These were estimated by the procedures described in Part VII. With the saturated sulphides, there was little variation in yields during the reaction. Results are tabulated.

O_2 absorbed	Thia*cyclo*hexane				2-Ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane		
Wt. %	0·30	0·56	0·92	1·64	0·30	0·95	1·93
Found as sulphoxide (%)	38	35	36	32	14	11	8
Found as water (%)	—	—	48	46	37	36	35

Aldehydic disulphide (I). This was estimated in three ways: (i) from the amount of 5-mercaptopentan-1-ol isolated from the reduction of residue (A) with lithium aluminium hydride; (ii) gravimetrically, from the chromatographically purified 2 : 4-dinitrophenylhydrazone obtained by reaction of residue (A) with Brady's reagent; and (iii) polarographically from the polarogram of residue (A) in 85 : 15 (v/v) acetone-free methanol–water containing 0·025M-tetramethylammonium bromide at a dropping-mercury cathode, the diffusion coefficient of these disulphide groups being assumed equal to that of *n*-butyl disulphide. The three methods gave values of 15·6, 14·3, and 18·0%, respectively, for the amount of (I) present in (A), and the mean value of 16% was used for the calculations in the Table below.

Oxo-disulphide (II) *and ketone* (III). These were estimated gravimetrically after chromatographic separation of the 2 : 4-dinitrophenylhydrazones obtained by reaction of residue (C) with Brady's reagent.

From these estimations the approximate distribution of the absorbed oxygen is as expressed below for thia*cyclo*hexane at an uptake of 1·43 wt.-% of oxygen and for 2-ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane at an uptake of 1·71 wt.-% of oxygen.

	Thia*cyclo*hexane			2-Ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane			
	H_2O	Sulphoxide	(I)	H_2O	Sulphoxide	(II)	(III)
O_2 absorbed (%)	47	35	13	36	11	9	26

Thiol groups. The thiol (0·1 milliequiv.) in 95% ethanol (100 ml.) was titrated with 0·00931N-silver nitrate, the end-point being determined amperometrically with a spinning platinum electrode and a calomel cell.[9]

We are indebted to Mr. G. Higgins for the spectroscopic data.

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[*Received, November 5th,* 1956.]

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[9] Kolthoff and Harris, *Ind. Eng. Chem. Analyt.*, 1946, **18**, 161.