

579. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part IX.* The Reaction of Sulphur with 2:6-Dimethylocta-2:6-diene.*

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Reaction of 2:6-dimethylocta-2:6-diene (I) with sulphur at 140° yields 2:6-dimethylocta-2:4:6-triene (II), the cyclic monosulphides (III)—(VI), and a cross-linked polysulphide fraction containing two diene (C₁₀) units joined by one or two sulphur cross-links. Increasing the reaction time leads to redistribution of the polysulphidic sulphur in terms of increasing the proportion of cyclic monosulphides and of converting acyclic cross-linked polysulphide into structures having cyclic units based on the skeletal structure of (IV) vicinal to shorter sulphur cross-links.

FARMER and SHIPLEY¹ showed that reaction of sulphur with 2:6-dimethylocta-2:6-diene (I) at 140° yields a cyclic monosulphide and a cross-linked polysulphide. No detailed investigation of the structures of these cyclic monosulphide or polysulphide products was undertaken, but it was deduced¹ that the former contained 6-ethyl-2:2:6-trimethylthiacyclohex-3-ene (VIII) and a compound having vinylidene unsaturation, CH₂:CRR', as apparently revealed by the infrared spectrum, and this has formed part of the evidence on which broad mechanistic conclusions have been based.²

This reaction has now been re-examined in greater detail; the compositions of the cyclic sulphide and cross-linked polysulphide fractions and their variation with time of reaction have been determined. Results and conclusions differing in important respects from those advanced by the earlier workers have been reached, as reported preliminarily elsewhere.³

Constitution of the Cyclic Sulphide Fraction.—This fraction contains 2:6-dimethylocta-2:4:6-triene (II) (*alloocimene*), two saturated cyclic sulphides (C₁₀H₂₀S) [2-ethyl-2:6:6-trimethylthiacyclohexane (III) and 2-ethyl-2-methyl-5-*isopropyl*thiacyclopentane

* Part VIII, preceding paper.

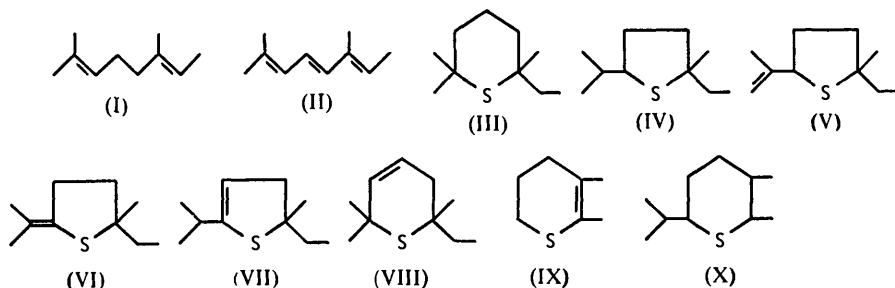
¹ Farmer and Shipley, *J.*, 1947, 1519.

² Farmer, *J. Soc. Chem. Ind.*, 1947, **66**, 86; Bloomfield and Naylor, Proc. XIth Internat. Congr. Pure Appl. Chem., London, 1947, Vol. II, p. 7; Bloomfield, Proc. 2nd Rubber Tech. Conf., London, 1948, p. 79.

³ Bateman, Glazebrook, Moore, and Saville, Proc. 3rd Rubber Tech. Conf., London, 1954, p. 298.

(IV)], and two monounsaturated cyclic sulphides [2-ethyl-2-methyl-5-isopropenyl- (V) and 2-ethyl-2-methyl-5-isopropylidene-thiacyclopentane (VI)].

The triene (II) and the cyclic sulphides (III)—(VI) were identified mainly by infrared and ultraviolet spectroscopic examination of the bulk cyclic sulphide and of constituent



fractions given by a combination of distillation, chromatography, and catalytic hydrogenation.

By a combination of fractional distillation and chromatography on alumina or silica gel, the triene (II) was removed from the cyclic sulphide mixture (which then gave analyses for a mixture of $C_{10}H_{18}S$ and $C_{10}H_{20}S$), and the latter partially resolved into (III)—(VI). The triene (II) was shown by spectroscopy to be predominantly the *trans*- C_4 , *cis*- C_6 isomer (cf. O'Connor and Goldblatt⁴) and was estimated by absorption at 2730 Å. The presence of the isomers (III) and (IV) in the cyclic sulphide mixture was established by comparison of the infrared absorption spectrum with those of synthetic (III) and (IV);⁵ chromatography gave a fraction which was devoid of (IV), (V), and (VI) and had an infrared spectrum identical with that of pure (III). Although isomers (V) and (VI) have not yet been synthesised (cf. Glazebrook and Saville⁵), evidence for their presence in the mixture can be adduced as follows. Infrared absorption at 1640 and 890 cm^{-1} in the bulk cyclic sulphide indicated vinylidene unsaturation, $CH_2:CRR'$; this is attributed to compound (V) since chromatography on silica gel gave a fraction which was free from (II) and (VI) and contained only minor amounts of (III) and (IV), but had *ca.* 50–60 mole % of $CH_2:CRR'$ groups, and on catalytic hydrogenation⁶ gave the pure thiophan (IV), as shown by direct comparison with a synthetic specimen. Evidence for the presence of compound (VI) is: (i) selective ultraviolet absorption at 2290–2300 Å, associated with the vinylic sulphide, $C:C-S-$, chromophore, also shown by the synthetic cyclic sulphide (IX);⁷ (ii) removal of ingredients (II), (III), (IV), and (V) by chromatography to give a fraction which had maximum absorption at 2290 Å (ϵ 7750) but had no infrared absorption attributable to olefinic unsaturation other than the tetrasubstituted type, and on catalytic hydrogenation absorbed hydrogen equivalent to 0.95 double bond per $C_{10}H_{18}S$ molecule to give the cyclic sulphide (IV). The presence of the skeletal structures of (III) and (IV) in the cyclic sulphide fraction was confirmed by conversion of the latter into a cyclic sulphone mixture, $C_{10}H_{18-20}O_2S$, which on catalytic hydrogenation absorbed hydrogen equivalent to 0.35 double bond per $C_{10}H_{18}O_2S$ molecule to give the sulphones of (III) and (IV).⁸

Contrary to Farmer and Shipley's report,¹ the cyclic sulphide (VIII) could not be detected. None of the cyclic sulphide fractions showed infrared absorption attributable to the *cis*- $R\cdot CH:CH\cdot R'$ grouping, as is observed at 715 cm^{-1} in the analogous 2 : 2 : 6 : 6-tetramethylthiacyclohex-3-ene.⁸ Spectroscopic analysis of all catalytically hydrogenated

⁴ O'Connor and Goldblatt, *Analyt. Chem.*, 1954, **26**, 1726.

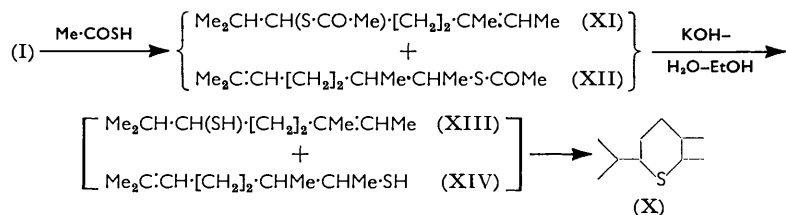
⁵ Glazebrook and Saville, *J.*, 1954, 2094.

⁶ Bateman and Shipley, *J.*, 2888.

⁷ Bateman and Glazebrook, *J.*, 2834.

⁸ Naylor, *J.*, 1949, 2749.

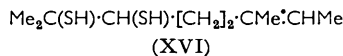
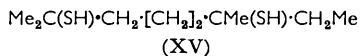
cyclic sulphide fractions also showed the absence of 2:3-dimethyl-6-isopropylthiacyclohexane (X). For comparative purposes, this compound was synthesised as illustrated:



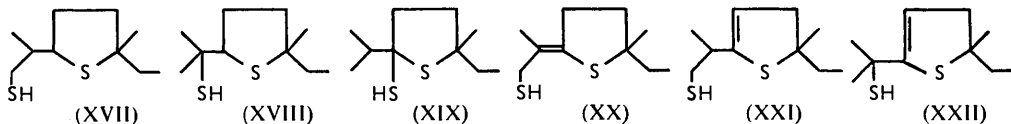
Certain of the cyclic sulphide fractions which had been subjected to considerable heating during distillation probably contained some 5-ethyl-5-methyl-2-isopropylthiacyclopent-2-ene (VII). However, this compound does not appear to be a primary reaction product but results from the sulphur- or polysulphide-catalysed isomerisation of (VI) (cf. p. 2850).

Constitution of the Cross-linked Polysulphide Fraction.—The polysulphide mixture obtained from the diene (I)–sulphur reaction at 140° has been less completely analysed, but it has been established that the composition varies considerably with the reaction time and that the cross-linked structures do not, as previously envisaged,^{1,2} consist solely of acyclic di-isoprene (C₁₀) units linked as alkenyl alkyl polysulphides but contain cyclic units based on the skeletal structure of (IV) at points vicinal to the polysulphide cross-link. More information about the polysulphide structures follows from fission of the –S–S– bonds with lithium aluminium hydride^{5,9} in conjunction with spectroscopic and elementary analyses of the original polysulphide and its hydrogenolysis products.

Analyses of the polysulphide obtained in a 5 hours' reaction indicated a composition (C₁₀H₁₈S_{2.9})_{1.82}; the product therefore consists mainly of two di-isoprene units linked by a polysulphide bridge and does not involve repetitive interlinking of diene units by sulphur atoms (cf. refs. 3 and 10). It has much less unsaturation than is required for an alkenyl alkyl polysulphide structure (3 double bonds per C₂₀ unit), there being only 0.5–1.0 RR'C:CHR'' group per molecule and smaller amounts (<0.05) of CH₂:CRR'' and possibly *trans*-R·CH:CH·R' groups (<0.1–0.2 per molecule); these findings suggest the presence of cyclic structures. Hydrogenolysis of the polysulphide yielded hydrogen sulphide (indicative of polysulphide cross-links), acyclic monothiol and dithiol, and mercaptocyclic sulphides [C₁₀H₁₈₋₂₀S₂ (1 SH)], together with a non-cleavable residue (Table 2, expt. 1).



The monothiol proved to be a mixture of a doubly unsaturated compound (C₁₀H₁₇·SH) and a monounsaturated compound (C₁₀H₁₉·SH), in which the unsaturation is mainly trialkylethylenic with smaller amounts of *trans*-R·CH:CH·R', CH₂:CRR', and C:C:C:C groups, and the thiol grouping mainly tertiary. The infrared spectrum of the dithiol fraction is consistent with the presence of the saturated dithiol (XV) or unsaturated

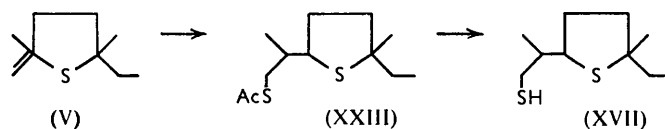


analogues thereof containing 1 double bond per C₁₀ unit, or with a 1:2-dithiol such as (XVI), comparable with the 1:2-dithiols obtained from hydrogenolyses of polysulphides from mono-olefins.¹⁰ The mercaptocyclic sulphide is largely saturated and appears to

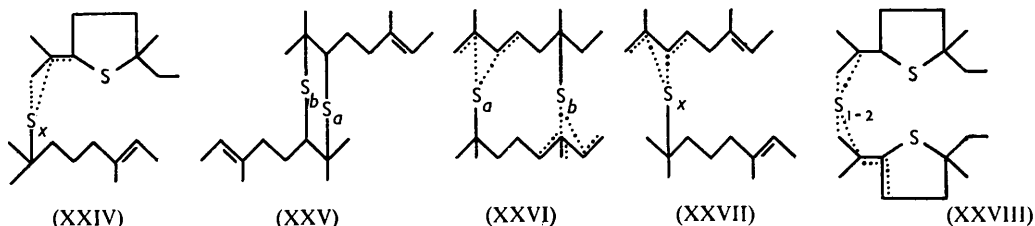
⁹ Arnold, Lien, and Alm, *J. Amer. Chem. Soc.*, 1950, **72**, 731.

¹⁰ Bateman, Glazebrook, Moore, Porter, Ross, and Saville, preceding paper.

consist of the thiophans (XVII) and (XVIII), with possibly (XIX), and minor amounts of their unsaturated analogues (XX), (XXI), and (XXII) containing the C:C-S- chromophore. For reference the mercaptocyclic sulphide (XVII) was prepared by the reaction sequence:



The preparation of the isomer (XVIII) has been previously described,⁵ but unambiguous syntheses of the mercaptocyclic sulphides (XIX)—(XXII) have not been realised. The uncleavable material is predominantly saturated, and contains cyclic structures based on (XVII)—(XXII), and smaller amounts of acyclic structures, cross-linked by monosulphide units.



The above results show that the polysulphide obtained after 5 hours' reaction is composed of both cyclic and acyclic units cross-linked by a mono- or poly-sulphide group as typified by (XXIV)—(XXVII) in which the dotted lines represent the alternative positions of the C-S and C:C bonds.

Analyses of the polysulphide obtained after 50 hours' reaction indicated a composition $(C_{10}H_{17.6}S_{1.46})_{1.74}$, incomplete removal of small amounts of the triene (II) and cyclic sulphides causing the slight departure from a C_{20} unit structure. It consisted essentially of the cross-linked sulphides (XXIV; $x = 1 - 2$) and (XXVIII). Hydrogenolysis yielded only 8% of the total sulphur as hydrogen sulphide, showing that cross-links greater than $-S_2-$ occurred only to a very small extent. The other hydrogenolysis products were mainly uncleavable material (67% of the original polysulphide), containing cyclic sulphide structures based on (XVII)—(XXII) joined by monosulphide cross-links, and mercaptocyclic sulphides $[C_{10}H_{18-20}S_2 (1-SH)]$ which consisted mainly of the saturated structures (XVII)—(XVIII), with smaller amounts of (XX)—(XXII).

Influence of Reaction Time on Diene (I)—Sulphur Reaction.—Increasing the reaction time from 5 to 50 hours leads to an increased yield of sulphurated product (Table I) (cf.

TABLE I. Reaction of 2 : 6-dimethylocta-2 : 6-diene (I) (100 g.) with sulphur (10 g.) at 140°.

Expt. no.	Reaction time (hr.)	Cyclic sulphide (A) (g.)	Poly-sulphide (B) (g.)	Triene (II) (g.)	A/B	Diene in A		S (%) in B	"Removable sulphur" in B *
						Diene in A	Diene in B		
1	5.0	5.0 †	20.6	0.48	0.42	0.56	40.0	52	
2	50.0	12.0 ‡	24.4	0.72	0.85	0.92	25.3	8	

* Removed as hydrogen sulphide on hydrogenolysis. † Contains (III) plus (IV), 48%; (V), 41%; (VI), 11%. ‡ Contains (III) plus (IV), 43%; (V), 26%; (VI), 30%; (VII) 1-2%.

Bloomfield¹¹ and Ross¹²) and a redistribution of the polysulphide sulphur, reflected in the decreased sulphur content of the polysulphide and the increased amount of cyclic sulphide in the total product. The compositions of the products also change markedly; the yield of the cyclic sulphide (VI) increases relatively to that of (V), although changes

¹¹ Bloomfield, *J. Soc. Chem. Ind.*, 1949, 68, 66.

¹² Ross, following paper.

in the proportions of the saturated cyclic sulphides (III) and (IV) are slight (Table 1). The two reasons for these changes are: first, the incorporation of the thiophan (V) into

TABLE 2. *Composition of polysulphide hydrogenolysis products (yield: wt. % of polysulphide).*

Reaction time (hr.)	Poly-sulphidic sulphur*	Cyclic sulphide $C_{10}H_{18-20}S$	Mono-thiol $C_{10}H_{17-19}SH$	Mercaptocyclic sulphide $C_{10}H_{18-20}S_2(1 SH)$	Dithiol $C_{10}H_{18-22}S_2(2 SH)$	Higher-boiling products	Loss
5 †	21	0	30	16	18	12	3
50	2	5 ‡	8	17	1	67	0

* Removable as hydrogen sulphide by hydrogenolysis. † Main fraction. ‡ Impurity in polysulphide.

polysulphide structures by interaction with sulphur and/or decomposing polysulphide (see below); secondly, the sulphur- or polysulphide-catalysed isomerisation of the compound (V) to (VI), analogous to the base-catalysed isomerisation of allylic (C:C:C-S-) to vinylic (C:C:C-S-) sulphides.¹³ The occurrence of these secondary reactions was confirmed by independent experiment; reaction of a cyclic sulphide fraction containing predominantly vinylidene unsaturation [due to (V)] with 10% of sulphur at 140° yielded a cross-linked polysulphide (~40% of the reactant mixture) consisting of cross-linked cyclic sulphides typified by (XXVIII), together with a cyclic sulphide fraction in which (VI) was the sole unsaturated species. Further, reaction of a cyclic sulphide containing 60% of (V) and only 4.5% of (VI) with a catalytic amount of sulphur (1.5%) for 48 hours at 140° yielded a cyclic sulphide containing 37% of (V) and 23% of (VI). No isomerisation of (V) to (VI) occurred when the cyclic sulphide was heated alone *in vacuo* for 48 hours at 140°. These reactions are further discussed in Part XI.

With the cross-linked polysulphide, increasing the reaction time leads to redistribution of the polysulphidic sulphur with a decrease in the cross-link to mainly $-S_1-$ and $-S_2-$ units and with more cyclic sulphide structures incorporated in the polysulphide (Tables 1 and 2). Similar changes were observed on heating the polysulphide, isolated after 5 hours' reaction, at 140° for 7 hours: this gave a small amount of cyclic sulphide, consisting mainly of (III) (~75%) with some (VI) ($\leq 27\%$) and a polysulphide which was largely saturated and contained an increased proportion of cyclic structures as present in (XXVIII).

EXPERIMENTAL

2 : 6-Dimethylocta-2 : 6-diene (I).—This was prepared by the reduction of purified geraniol,¹⁴ and had b. p. 56.0°/14 mm., n_D^{20} 1.4520.

Synthesis of Cyclic Sulphides.—Compounds (III) and (IV) were prepared as described by Glazebrook and Saville.⁵ The thiacyclopentane (IV) formed a *mercuric chloride complex*, m. p. 115—116° (Found: C, 26.9; H, 4.7; Cl, 15.6, 15.65; Hg, 45.2. $C_{10}H_{20}S.HgCl_2$ requires C, 27.0; H, 4.5; Cl, 16.0; Hg, 45.3%).

2 : 3-Dimethyl-6-isopropylthiacyclohexane (X). The 1 : 5-diene (I) (55 g.) reacted exothermically with mercaptoacetic acid (15.2 g.) at room temperature; the reaction was completed on the steam-bath (30 min.) and the product then fractionated to give a mixture of mercaptoacetates (XI) and (XII), b. p. 126—128°/10 mm., n_D^{20} 1.4828 (28 g., 66%) (Found: C, 67.0; H, 10.25; S, 15.1. Calc. for $C_{12}H_{22}OS$: C, 67.3; H, 10.3; S, 14.95%). This (28 g.) was refluxed under nitrogen with potassium hydroxide (20 g.) in water (100 ml.) and ethanol (100 ml.) for 15 min., and the cooled solution was diluted with water (500 ml.), acidified with acetic acid, extracted with ether, dried, and fractionated, then having b. p. 92—94°/10 mm., n_D^{20} 1.4800 (17 g., 71%) (Found: C, 69.3; H, 11.4; S, 18.3; thiol-S, 10.2. Calc. for $C_{10}H_{18}SH$: C, 69.8; H, 11.6; S, 18.6; thiol-S, 18.6%). This product in *cyclohexane* was cooled in running water and irradiated with ultraviolet light for 2 hr. (until the thiol content fell to zero); fractionation then gave compound (X), b. p. 86—89°/8 mm., n_D^{20} 1.4805 (Found: C, 70.3; H, 11.8;

¹³ Tarbell and McCall, *J. Amer. Chem. Soc.*, 1952, **74**, 48; Tarbell and Lovett, *ibid.*, 1956, **78**, 2259.

¹⁴ Chablay, *Ann. Chim. (France)*, 1917, **8**, 145; Dupont, Dulou, and Desreux, *Bull. Soc. chim. France*, 1939, **6**, 84.

S, 18.3. Calc. for $C_{10}H_{20}S$: C, 69.8; H, 11.6; S, 18.6%), which had an infrared spectrum similar to that of a specimen prepared by Naylor.¹⁵

Determination of Thiols.—The thiol in ethanol was titrated against standard aqueous silver nitrate and the end-point determined by the amperometric method.¹⁶ In earlier work the thiol was determined by titration against a standard butanol solution of copper butyl phthalate;¹⁷ such determinations are designated C.B.P. below.

Spectrometric Analyses.—(i) *Cyclic sulphide fractions.* The amounts of triene (II) and the cyclic sulphides (III)—(VII) in these were determined as follows: (a) The triene (II) by absorption at 2730 Å in EtOH; $\epsilon = 42,870$ at 2730 Å for pure (II);⁴ (b) (III) by means of a sharp band of medium intensity at 872 cm^{-1} characteristic of synthetic (III) (this determination is satisfactory except where large amounts of CH_2CRR' groups, which absorb strongly at 890 cm^{-1} , are present); (c) (V) by absorption at 890 cm^{-1} ; ϵ determined for 2-methylnon-1-ene and 2:4:4-trimethylpent-1-ene under comparable conditions; (d) (VI) by absorption at 2290 Å; $\epsilon = 7750$ at 2290 Å in EtOH found for fraction (Avii) (Table 4) which is assumed to be pure (VI) [this method is applicable only when (VII) is absent]; (e) when (VI) and (VII) are both present approximate estimates were obtained from equations correlating the absorption of pure (VI) and of 2-methyl-5-isopropylthiacyclopent-2-ene⁷ (λ_{max} , 2400 Å; ϵ 2800 in EtOH) at 2290 and 2400 Å with the experimentally observed absorption of the cyclic sulphide mixture at these wavelengths; (f) (IV) was estimated by difference since pure (IV) lacks a distinctive band of sufficient intensity to permit estimation in mixtures.

(ii) *Polysulphide fractions.* The types and amounts of olefinic unsaturation in these were determined as described in Part VIII.¹⁰ Identification of the types of C-S linkages was based on spectroscopic characteristics of relevant synthetic sulphides and polysulphides (Higgins, unpublished data).

Reaction of 2:6-Dimethylocta-2:6-diene (I) with Sulphur.—(1) *Preliminary investigation.* A mixture of the olefin (466 g.) and sulphur (120 g.) was heated with stirring under nitrogen for 52 hr. at 140°. Fractional distillation then gave (i) unchanged olefin (120 g.), b. p. 55—57°/10 mm., n_D^{20} 1.4490; (ii) a small intermediate fraction (16 g.), b. p. 57—85°/10 mm., n_D^{20} 1.4840; (iii) a cyclic sulphide fraction (150 g.), b. p. 85—95°/10 mm., n_D^{20} 1.4870; and (iv) an undistillable polysulphide residue (300 g.).

Examination of the cyclic sulphide fraction (iii). Refractionation through a glass-helix-packed Fenske column gave three approximately equal fractions: (iiia) b. p. 84—90°/10 mm., n_D^{20} 1.4840 (Found: C, 69.25, 68.9; H, 11.2, 11.2; S, 18.2; C: H, 10:19.3, 19.4. Calc. for $C_{10}H_{18}S$: C, 70.5; H, 10.65; S, 18.85. Calc. for $C_{10}H_{20}S$: C, 69.8; H, 11.6; S, 18.6%); (iiib) b. p. 90—92°/10 mm., n_D^{20} 1.4839 (Found: C, 69.85, 69.85; H, 11.3, 11.55; S, 18.65%; C: H, 10:19.3, 19.7); (iiic) b. p. 92—94°/10 mm., n_D^{20} 1.4934 (Found: C, 69.4, 69.95; H, 10.3, 10.65; S, 18.65%; C: H, 10:17.7, 18.2). Fractions (iiib and c) were combined, and a portion was dissolved in light petroleum and eluted through alumina under nitrogen; the solvent was removed from the eluate and the products were distilled, to give cyclic sulphide (A), b. p. 82—90°/10 mm., n_D^{19} 1.4875 (Found: C, 70.75; H, 11.6; S, 18.3%), containing a little of the solvent. Repetition of the above procedure with a further portion of the combined fractions (iiib) and (iiic) gave cyclic sulphide (B), b. p. 88—90°/10 mm., n_D^{19} 1.4880 (Found: C, 70.3; H, 11.25; S, 18.7%; C: H, 10:19.1). Spectroscopic analysis of (A) indicated approximately 0.7% of the triene (II), 30% of (III), 4% of (V), 27% of (VI), 14% of (VII) and 24% (by difference) of (IV). The product (A) in light petroleum was rechromatographed on alumina and then distilled, to give cyclic sulphide (Ai), b. p. 83—86°/10 mm., n_D^{20} 1.4867 (Found: C, 69.8; H, 11.1; S, 18.5%; C: H, 10:19.0), which on catalytic hydrogenation⁶ absorbed 0.35 H_2 per $C_{10}H_{18}S$ unit. Distillation of the reduction product gave: (Aii), b. p. 82—85°/10 mm., n_D^{20} 1.4791 (Found: C, 69.2; H, 11.45; S, 18.8%; C: H, 10:19.7), which contained (III) and (IV) in approximately equal proportions, but not the thiacyclohexane (X); ultraviolet absorption indicated a maximum of 2% (VI) plus (VII). Cyclic sulphide (B) absorbed 0.38 H_2 per $C_{10}H_{18}S$ unit and gave the product (Bii), b. p. 82—85°/10 mm., n_D^{20} 1.4796 (Found: C, 69.85; H, 11.25; S, 18.7%), which was mainly (IV) (90—95%) with a little (III), there being no (X) and only a trace of unsaturated groups revealed by a very weak band at ~ 1640 cm^{-1} . Treatment of product (Bii) with mercuric chloride gave the mercurichloride derivative of (IV), m. p. and

¹⁵ Naylor, J., 1947, 1532.

¹⁶ Kolthoff and Harris, *Ind. Eng. Chem. Analyt.*, 1946, **18**, 161.

¹⁷ Turk and Reid, *Ind. Eng. Chem. Analyt.*, 1945, **17**, 713.

mixed m. p. 117° (Found: C, 27.0; H, 4.6; Hg, 45.4. Calc. for $C_{10}H_{20}S, HgCl_2$: C, 27.0; H, 4.5; Hg, 45.3%). The apparent disparity in the relative amounts of (III) and (IV) present in samples (*AiH*) and (*BH*) suggests the non-identity of their respective precursors and this was in part confirmed when infrared analysis of cyclic sulphide (*B*) revealed 16% of (V) and probably <25% of (III). These results indicate partial separation of the components in combined fractions (*iiib* and *c*) to different extents during chromatography and distillation, confirmed by the distillative and chromatographic separations of the components of cyclic sulphide (*A*) described below.

Distillative fractionation of cyclic sulphide (A). Fractionation of sample (*A*) (20 ml.) through a concentric-tube column gave the fractions listed in Table 3.

TABLE 3. Compositions of fractions derived from cyclic sulphide (*A*).

Fraction no.	B. p./mm.	Vol. (ml.)	n_D (temp.)	Formula	Composition (wt. %)				
					(III)	(IV)	(V)	(VI)	(VII)
(<i>Aii</i>)	131—133°/83—84	4	1.4851 (19.5°)	$C_{10}H_{18.6}S$	35	0	0	43	35
(<i>Aiii</i>)	133—138°/83—84	6	1.4837 (19°)	$C_{10}H_{19.7}S$	72	16*	0	12	—
(<i>Aiv</i>)	138—139°/83—84	5	1.4834 (19°)	$C_{10}H_{19.7}S$	55	32*	6	8	—
(<i>Av</i>)	105—110°/10	0.5	1.4951 (22°)	$C_{10}H_{18.4}S$	≤25	0	8	63	Trace
(<i>Avi</i>)	110—115°/10	0.5	1.5010 (21.5°)	$C_{10}H_{18.1}S$	Trace	Trace	7	80	Trace

* By difference.

Chromatographic fractionation of cyclic sulphide (A). A sample in light petroleum was chromatographed on silica gel (100—200 mesh) and eluted with the same solvent. Four approximately equal fractions were obtained which, after removal of solvent, gave the cyclic sulphide fractions whose compositions are given in Table 4. Confirmation that fraction (*Avii*) was substantially pure (VI) was the absorption of 0.95 H_2 per $C_{10}H_{18}S$ unit, to give a cyclic sulphide (*AviiH*) consisting of substantially pure (IV) with a maximum of 2% of (VI) and no (III), (V), or (X).

TABLE 4. Cyclic sulphides (%) in fractions derived from cyclic sulphide (*A*) by chromatographic separation.

Fraction no.	n_D^{20}	(III)	(IV)	(V)	(VI)
(<i>Avii</i>)	1.5049	0	0	0	100
(<i>Aviii</i>)	1.4885	0	50—60	8	40
(<i>Aix</i>)	1.4828	35	55	7	6
(<i>Ax</i>)	1.4822	100	0	0	—

Oxidation of cyclic sulphide (Ai) to sulphone. Cyclic sulphide (*Ai*) (8.8 g.) on oxidation with hydrogen peroxide-acetic acid at 0° gave sulphone (*AiS*), b. p. 92—94°/0.01 mm., n_D^{20} 1.4880 (8.4 g., 80%) (Found: C, 58.95; H, 9.5; S, 15.55; C : H, 10 : 19.2. Calc. for $C_{10}H_{18}O_2S$: C, 59.5; H, 8.9; S, 15.85. Calc. for $C_{10}H_{20}O_2S$: C, 58.9; H, 9.8; S, 15.7%), which absorbed 0.35 H_2 per $C_{10}H_{18}O_2S$ molecule, to give a saturated sulphone (*AiSH*), b. p. 78—79°/0.01 mm., n_D^{20} 1.4836 (Found: C, 58.9; H, 9.8; S, 15.65%; C : H, 10 : 19.8). This consisted of the sulphone derivatives of (III) (47%) and (IV) (53%).

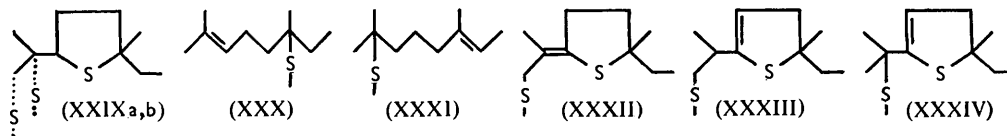
Reaction of 2 : 6-Dimethylocta-2 : 6-diene (I) with Sulphur.—(2) 50 hours' reaction. A mixture of the olefin (90.0 g.) and sulphur (9.0 g.) was heated *in vacuo* for 50 hr. at 140°. Fractional distillation then gave unchanged olefin, a cyclic sulphide fraction (*C*), b. p. 88—94°/10 mm., n_D^{20} 1.4950 (20.5 g.) (Found: C, 71.5; H, 11.2; S, 16.9%; C : H, 10 : 18.7), and a polysulphide residue (*D*) (21.9 g.) involatile at 60°/0.001 mm. [Found: C, 64.7; H, 9.55; S, 25.3%; *M*, 313, 327. Corresponds to $(C_{10}H_{17.6}S_{1.46})_{1.74}$]. Fraction (*C*) contained approximately 7% of the triene (II), 24% of (V), 28% of (VI), 1—2% of (VII), and (III) and (IV) in roughly equal proportions.

Hydrogenolysis of polysulphide (D). The polysulphide (*D*) (10.0 g.) in tetrahydrofuran (50 ml.) was added to lithium aluminium hydride (3 g.) in tetrahydrofuran (100 ml.) and the mixture refluxed for 6 hr. The product was decomposed with 2*N*-sulphuric acid (100 ml.) at 0° and the evolved hydrogen sulphide removed in a current of nitrogen and collected in aqueous lead acetate to give lead sulphide (1.5 g.; *i.e.*, 8% of "removable sulphur"). The hydrogenolysis products were extracted with light petroleum and fractionated, to give: (*Di*), b. p. <55°/0.01 mm., n_D^{20} 1.5073 (1.05 g.) (Found: C, 66.8; H, 10.15; S, 22.1; thiol-S, 11.5%; C : H, 10 : 18.1; *M*, 176, 190); (*Dii*), b. p. 55—57°/0.01 mm., n_D^{20} 1.5189 (0.96 g.) (Found:

C, 64.7; H, 9.9; S, 25.9; thiol-S, 13.7%; C : H, 10 : 18.2; *M*, 183, 196); (*Diii*), b. p. 57—60°/0.01 mm., n_D^{20} 1.5236 (1.12 g.) [Found: C, 60.5; H, 9.7; S, 29.55; thiol-S, 18.1%; C : H, 10 : 19.1; *M*, 199, 213. Calc. for $C_{10}H_{18}S_2$ (1SH): C, 59.5; H, 8.9; S, 31.7; thiol-S, 15.8%; *M*, 202. Calc. for $C_{10}H_{20}S_2$ (1SH): C, 58.8; H, 9.8; S, 31.4; thiol-S, 15.6%; *M*, 204]; (*Div*), b. p. <100°/0.001 mm., n_D^{20} 1.5336 (4.16 g.) [Found: C, 67.3; H, 10.05; S, 22.25; thiol-S, 6.75%; C : H, 10 : 17.8; *M*, 287, 300. Corresponds to $(C_{10}H_{17.8}S_{1.24})_{1.66}$]; and (*Dv*) an undistillable residue (*ca.* 2.5 g.), not further examined. The sulphur and thiol contents of the above fractions together with their molecular weights permitted the determination of the amounts of monothiol, dithiol, and mercaptocyclic sulphide formed (Table 2).

A second polysulphide (*Da*) (Found: C, 61.5; H, 9.3; S, 29.2%), comparable to polysulphide (*D*), was obtained by evaporative distillation at <110°/10⁻³ mm. of the polysulphide residue obtained from reaction of (*I*) with sulphur for 52 hr. at 140° (section 1, p. 2851). Hydrogenolysis of polysulphide (*Da*) (16.0 g.) gave negligible hydrogen sulphide and the following fractions: (*Dai*), b. p. <60°/0.01 mm., n_D^{20} 1.5041 (1.4 g.) [Found: C, 62.3; H, 10.2; S, 27.3; thiol-S (C.B.P. method), 16.2%; C : H, 10 : 19.5; *M* (cryoscopic in C_6H_6), 188]; (*Daii*), b. p. 60°/0.01 mm., n_D^{20} 1.5160 (2.7 g.) [Found: C, 60.15; H, 9.85; S, 29.95; thiol-S (C.B.P. method), 15.8%; C : H, 10 : 19.5; *M*, 203, 208]; (*Daiii*), b. p. 60°/0.01 mm., n_D^{20} 1.5210 (2.7 g.) [Found: C, 59.9; H, 9.6; S, 30.9; thiol-S (C.B.P. method), 16.4%; C : H, 10 : 19.1; *M*, 202, 203. Calc. for $C_{10}H_{18}S_2$ (1 SH): C, 59.35; H, 8.95; S, 31.7; thiol-S, 15.85%; *M*, 202.4. Calc. for $C_{10}H_{20}S_2$ (1SH): C, 58.75; H, 9.9; S, 31.35; thiol-S, 15.7%; *M*, 204.4]; (*Daiv*), b. p. 60°/0.01 mm., n_D^{20} 1.5278 (1.4 g.); and (*Dav*), residue (6.0 g.) which on molecular distillation at 60—105°/10⁻³ mm. gave: (*Davi*), n_D^{18} 1.5340 [Found: C, 65.4; H, 9.95; S, 24.25; thiol-S (C.B.P. method), 5.6%; *M*, 310. Corresponds to $(C_{10}H_{18.1}S_{1.39})_{1.70}$]; (*Davii*), n_D^{18} 1.5350 [Found: C, 66.45; H, 10.05; S, 23.2; thiol-S (C.B.P. method), 3.0%; *M*, 322, 328. Corresponds to $(C_{10}H_{18.0}S_{1.31})_{1.81}$]; and (*Daviii*), n_D^{18} 1.5400 [Found: C, 66.6; H, 9.9; S, 23.8; thiol-S (C.B.P. method), 1.9%; *M*, 365. Corresponds to $(C_{10}H_{17.7}S_{1.34})_{2.02}$].

Spectroscopic Examination of Polysulphides (D) and (Da) and Their Hydrogenolysis Products.—Sample (*D*) showed weak infrared absorption bands attributable to minor contamination with cyclic sulphide and triene (*II*), which is also indicated by the analyses of the polysulphide and its hydrogenolysis products (*Di*) and (*Dii*), and by ultraviolet absorption thereof at 2300—2350 and 2800 Å, attributed to ~6—10% of (*VI*) and ≤2% of (*II*), respectively. The infrared spectrum of (*Da*) resembled that of the mercaptocyclic sulphide (*XVIII*), suggesting that (*Da*) consists essentially of cyclic sulphide units cross-linked by sulphur atoms, and this accords with the analysis of the hydrogenolysis products (*Dai*)—(*Daiv*). The spectra of the latter resemble that of the tertiary mercaptocyclic sulphide (*XVIII*) more than that of the primary mercaptanalogue (*XVII*). The higher-boiling hydrogenolysis fractions (*Davi*—*viii*), substantially devoid of thiol groups, are spectroscopically similar to (*XVIII*); apart from weak infrared absorption attributed to 0.3—0.6 RR'C:CHR' group per molecule, these samples appear to be saturated. However, they show maximum ultraviolet absorption at 2350—2360 Å attributed to C:C-S groups [(*Davi* and *vii*), ~0.45; (*Daviii*), ~0.6]. Similarly, the major hydrogenolysis fraction (*Div*) of polysulphide (*D*) showed maximum ultraviolet absorption at 2400 Å, indicating ~0.6 C:C-S group per molecule. It is thus inferred that the fractions (*Davi*—*viii*) contain structures (*XXIX*)—(*XXXIV*). Since structures (*XXXIII*) and (*XXXIV*) contain trisubstituted double bonds and as there is an apparent correlation between the amounts of C:C-S and RR'C:CHR' groups the observed absorption in (*Davi*—*viii*) at ~830 cm.⁻¹ may be associated solely with structures (*XXXIII*) and (*XXXIV*).



Reaction of 2:6-Dimethylocta-2:6-diene (I) with Sulphur.—(3) 5 hours' reaction. A mixture of the olefin (200 g.) and sulphur (20.0 g.) was heated *in vacuo* for 5 hr. at 140°. The product was cooled at -20° overnight, sulphur (7.0 g.) which had separated was filtered off, and the filtrate fractionated, to give (i) unchanged olefin (168 g.) which contained 2.7% of $CH_2:CRR'$ - and 2.1% of $CH_2:CHR'$ -type unsaturation in addition to the original trialkylethylene unsaturation, (ii) a

cyclic sulphide fraction (12.0 g.), collected at 0.1 mm. (bath-temp. at 80—90°) in a trap cooled in acetone-carbon dioxide; and (iii) a polysulphide residue (24.0 g.).

Examination of the cyclic sulphide fraction (ii). Distillation gave a main cyclic sulphide fraction (*E*), b. p. 82—88°/10 mm., n_D^{20} 1.4968 (Found: C, 72.2; H, 10.9; S, 15.65%; C : H, 10 : 18.0) which contained triene (II) 8%, (V) 38%, (VI) \approx 10%, and roughly equal amounts of (III) and (IV); no reliable estimate of (III) was possible owing to the large amount of (V) which masks absorption at 874 cm⁻¹. Cyclic sulphide fractions comparable to (*E*) gave similar analyses: for example, a cyclic sulphide fraction (*F*), b. p. 85—95°/10 mm., n_D^{20} 1.4970 (Found: C, 71.7; H, 10.9; S, 16.45%), contained triene (II) 9.3%, (V) 35—40%, (VI) 15%, and (III) and (IV). Attempts to hydrogenate the cyclic sulphide fraction catalytically failed owing to thiol formation and poisoning of the catalyst (cf. Bateman and Shipley⁶). Fractional elution of cyclic sulphide (*E*) in light petroleum through a silica-gel column gave main fractions: (*Ei*), n_D^{20} 1.5300; (*Eii*), n_D^{20} 1.5001; (*Eiii*), n_D^{20} 1.4902; (*Eiv*), n_D^{20} 1.4908; (*Eiv*), n_D^{20} 1.4897; (*Evi*), n_D^{20} 1.4897. Fraction (*Ei*) contained 73.6% of the *trans*-C₄, *cis*-C₆-triene (II), as indicated by ultraviolet absorption at 2730 Å; identification of other components was not possible because of the large amount of (II) present, but (V) and a small amount of (VI) were probably present. Fraction (*Eii*) contained (II) 12%, (V) ~50%, and (VI) ~20%. Fractions (*Eiii*—*vi*) had similar spectra; (*Eiii*) contained 54% of (V) and the other fractions ~50—60% of this compound; the ultraviolet spectra showed a maximum of ~1% of conjugated material [*i.e.*, (II) and (VI)] to be present in these fractions; identification of other compounds was hampered by the large amount of (V) present. Fractions (*Eiii*—*vi*) were combined (1.7 g.) (Found: C, 70.2; H, 11.0; S, 18.2%; C : H, 10 : 18.65); it did not absorb hydrogen catalytically. The cyclic sulphide (1.13 g.) was recovered and a portion (0.85 g.) catalytically hydrogenated; 0.93 H₂ per C₁₀H₁₈S molecule was absorbed, to give a cyclic sulphide (*Eiii*—*viH*), b. p. 80—90°/10 mm., n_D^{20} 1.4728, shown spectroscopically to be almost pure (IV) and confirmed by the formation of the mercurichloride derivative of (IV), m. p. and mixed m. p. 115—116°.

Examination of the polysulphide fraction (iii). A portion (20 g.) in light petroleum was eluted through alumina. After evaporation and removal of a little sulphur, the residue was heated at 60—80°/0.1 mm. for several hours to give a small distillate (Found: C, 59.2; H, 8.75; S, 31.95%; C : H, 10 : 17.6) and a main polysulphide residue (*G*) [Found: C, 51.75; H, 7.8; S, 40.0%; *M*, 414, 428. Corresponds to (C₁₀H₁₈S_{2.9})_{1.82}].

Hydrogenolysis of (*G*) (10.0 g.) as above gave hydrogen sulphide (equiv. to 52% of "removable sulphur") and fractions: (*Gi*), b. p. <95°/10 mm., n_D^{20} 1.4840 (0.39 g.) (Found: C, 71.75; H, 11.45; S, 16.5; thiol-S, 16.2%; C : H, 10 : 19.0); (*Gii*), b. p. 90—96°/10 mm., n_D^{20} 1.4890 (2.25 g.) (Found: C, 70.1; H, 11.0; S, 18.6; thiol-S, 19.4%; C : H, 10 : 18.7. Calc. for C₁₀H₁₈S: C, 70.5; H, 10.65; S, 18.85; thiol-S, 18.8. Calc. for C₁₀H₂₀S: C, 69.8; H, 11.6; S, 18.6; thiol-S, 18.6%); (*Giii*), b. p. 56—60°/0.01 mm., n_D^{20} 1.5140 (1.16 g.) (Found: C, 62.2; H, 9.7; S, 27.6; thiol-S, 21.9%; C : H, 10 : 18.6); (*Giv*), b. p. 60°/0.01 mm., n_D^{20} 1.5218 (2.66 g.) (Found: C, 59.35; H, 9.7; S, 30.85; thiol-S, 23.7, 24.0%; C : H, 10 : 19.5; *M*, 224. Calc. for C₁₀H₂₀S₂: C, 58.8; H, 9.8; S, 31.4; 1 thiol-S, 15.6; *M*, 204); (*Gv*), a residue (1.27 g.) which was evaporatively distilled at 140°/0.01 mm. to give (*Gvi*), n_D^{20} 1.5377 (0.61 g.) [Found: C, 64.0; H, 9.75; S, 25.5; thiol-S, 7.8, 8.1%; *M*, 383. Corresponds to (C₁₀H_{18.2}S_{1.49})_{2.06}], and (*Gvii*), a residue (*ca.* 0.6 g.) [Found: C, 60.3; H, 10.6; S, 27.4; thiol-S, 3.0%. Corresponds to (C₁₀H_{20.9}S_{1.7})_n].

Spectroscopic examination of polysulphide (G) and its hydrogenolysis products. The infrared spectrum of polysulphide (*G*) indicated that it was more unsaturated than the polysulphides (*D*) and (*Da*), and this was confirmed by comparison of their ultraviolet spectra, *viz.*, higher absorption in (*G*) at 2150—2500 Å, attributable to isolated C:C groups or singly conjugated structures. The unsaturation was predominantly of the RR'C:CHR'' type, absorption at 824 cm⁻¹ indicating 0.5—1.0 double bond per molecule. There was evidence of *trans*-R·CH:CH·R' groups (<10—20%), but the presence of saturated cyclic sulphide structures which also absorb at ~960 cm⁻¹ precluded an accurate estimate. Despite the lack of well-defined bands in the infrared spectrum of (*G*) to allow the types of C-S links present to be definitely identified, it was concluded that the polysulphide had a complex acyclic-cyclic sulphide structure.

The hydrogenolysis fractions (*Gi*) and (*Gii*) contained approximately the same amounts and types of unsaturation (RCH:CR'R'', 1.5 per mole; RCH:CHR', 0.1; CH₂:CR'R'', 0.1; C:C:C, 0.1). The infrared spectra of both fractions indicated the presence of a saturated

tertiary thio-group, $\text{Me}_2\text{C}(\text{S}-)\text{R}$; weak bands at 1240 cm.^{-1} suggested that small amounts of primary or secondary thiols may also be present. Fractions (Giii and iv) were more saturated than (Gi and ii); they could both contain the mercaptocyclic sulphides (XVII), (XVIII), and (XIX), the intensities of relevant infrared bands indicating a total of $\sim 50\%$ of these structures in agreement with the elementary analytical data. Ultraviolet absorption at $2390\text{--}2420\text{ \AA}$ in (Giv) probably indicates both $\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{C}$ and $\text{C}\cdot\text{C}\cdot\text{S}^-$ chromophores, the latter being associated with mercaptocyclic sulphide structures such as (XX), (XXI), and (XXII). The maximum amounts of the above chromophores are $5\text{--}5.5\%$ of the former or 19% of the latter. (Gvi) was similar to (Giv) and contained only a small amount of unsaturation which was mainly trialkylethylenic; it contained an appreciable amount of cyclic sulphide structures possessing the skeletal structure of the thiacyclopentane (IV). Sharp-maximum ultraviolet absorption at 2400 \AA in (Gvi) could be due to $0.75\text{ C}\cdot\text{C}\cdot\text{S}^-$ group or to $0.44\text{ C}\cdot\text{C}\cdot\text{C}\cdot\text{C}$ group per molecule.

Thermal Treatment of Polysulphide.—A sample (5.0 g.) of a polysulphide (Ga), similar to (G) [Found: C, 51.9; H, 7.95; S, 40.2%; M , 407, 413. Corresponds to $(\text{C}_{10}\text{H}_{18.3}\text{S}_{2.9})_{1.77}$], which had been freed from cyclic sulphide by 5 hours' heating at $60^\circ/0.001\text{ mm.}$, was heated *in vacuo* for 7 hr. at 140° , the material becoming darker and more viscous. The product was eluted through alumina with light petroleum, and the eluate fractionated at $90^\circ/0.1\text{ mm.}$, to give cyclic sulphide (H) (0.41 g.), $n_{\text{D}}^{20} 1.4846$ (Found: C, 71.6; H, 11.0; S, 16.8%; C : H, 10 : 18.3), containing (III) $\sim 75\%$, and (VI) (max. amount 27%); the material also showed very weak maximum absorption at 2820 \AA ($E_{1\text{cm.}}^{1\%}$ 45), which may be due to a small amount of highly conjugated material. The residual polysulphide (Ia) (2.64 g.) [Found: C, 52.35; H, 8.55; S, 40.1%; M , 430, 431. Corresponds to $(\text{C}_{10}\text{H}_{19.5}\text{S}_{2.87})_{1.86}$] yielded no further distillate from a pot-still at $100^\circ/0.01\text{ mm.}$ in 1 hr. Stripping the alumina column with chloroform gave polysulphide (Ib) (1.62 g.) [Found: C, 51.3; H, 7.3; S, 39.9%; M , 503, 509. Corresponds to $(\text{C}_{10}\text{H}_{17}\text{S}_{2.9})_{2.2}$]. The infrared spectra of polysulphides (Ia) and (Ib) were similar and suggested that both samples are nearly saturated, those bands in (Ga) assigned to trialkylethylenic groups having practically disappeared; between 1150 and 900 cm.^{-1} the spectra of (Ia) and (Ib) are similar to those of both mercaptocyclic sulphides (XVII) and (XVIII). Ultraviolet absorption of (Ib) at $2150\text{--}3000\text{ \AA}$ was less than that of (Ga), the greatest difference occurring at $2450\text{--}2500\text{ \AA}$; this decrease is ascribed to a decrease in content of conjugated structures.

Synthesis of Mercapto-cyclic Sulphide (XVII).—The cyclic sulphide mixture used had $n_{\text{D}}^{20} 1.4924$ (Found: C, 70.15; H, 11.2; S, 18.6%; C : H, 10 : 19.0). It was free from triene (II) and contained (V) 55%, (VI) $\succ 7\%$, and (III) and (IV) (total $\sim 38\%$ by difference). A mixture of the sulphide (1.8 g.) and redistilled mercaptoacetic acid (5 g.) was irradiated with ultraviolet light in a quartz tube *in vacuo*. Removal of unchanged acid and fractionation gave fractions: (i), b. p. $29\text{--}30^\circ/0.01\text{ mm.}$, $n_{\text{D}}^{20} 1.4890$ (0.31 g.) (Found: C, 68.75; H, 11.35; S, 19.3%; C : H, 10 : 19.7) which contained only (III) (67% based on a band at 874 cm.^{-1}) and (IV); (ii), b. p. $<103^\circ/0.01\text{ mm.}$ (0.1 g.); and (iii), b. p. $103\text{--}105^\circ/0.01\text{ mm.}$, $n_{\text{D}}^{20} 1.5207$ (1.58 g.), predominantly 5-(2-acetylthio-1-methylethyl)-2-ethyl-2-methylthiacyclopentane (XXIII) (Found: C, 58.65; H, 9.0; S, 25.7. $\text{C}_{12}\text{H}_{22}\text{OS}_2$ requires C, 58.5; H, 8.95; S, 26.0%). Hydrolysis of the thioester (iii) (1.0 g.) with boiling aqueous-ethanolic potassium hydroxide under nitrogen gave 2-ethyl-5-(2-mercapto-1-methylethyl)-2-methylthiacyclopentane (XVII), b. p. $65^\circ/0.01\text{ mm.}$, $n_{\text{D}}^{20} 1.5214$ (0.76 g., 92%) (Found: C, 59.1; H, 9.8; S, 31.3; thiol-S, 17.0, 17.1%; C : H, 10 : 19.8. $\text{C}_{10}\text{H}_{20}\text{S}_2$ requires C, 58.85; H, 9.8; S, 31.35; thiol-S, 15.6%), which gave a red colour with the Rheinboldt test indicating a primary or secondary thiol.

Sulphur-catalysed Thermal Isomerisation of Cyclic Sulphide (V).—The cyclic sulphide had b. p. $98\text{--}100^\circ/18\text{ mm.}$, $n_{\text{D}}^{20} 1.4895$ (Found: C, 70.35; H, 11.0; S, 18.9%; C : H, 10 : 18.7) and contained 60% of (V), 4.5% of (VI), and (IV), but no triene (II). It was unchanged at $140^\circ \pm 0.1^\circ$ *in vacuo* for 48 hr. The sulphide (0.5276 g.) and sulphur (7.8 mg.) were heated *in vacuo* at $140^\circ \pm 0.1^\circ$ for 48 hr. Evaporative distillation *in vacuo* of a portion (0.33 g.) of the product, $n_{\text{D}}^{20} 1.4979$, gave (i), a cyclic sulphide fraction, $n_{\text{D}}^{20} 1.4910$ (0.30 g.) (Found: C, 70.5; H, 11.2; S, 18.35, 18.8%; C : H, 10 : 19.0), $\lambda_{\text{max.}}$ 2290 \AA ($E_{1\text{cm.}}^{1\%}$ 113) in EtOH, and (ii) a polysulphide residue (0.03 g.) [Found: C, 61.65; H, 9.1; S, 29.15%. Corresponds to $(\text{C}_{10}\text{H}_{17.6}\text{S}_{1.77})_n$]. If the polysulphide (ii) results from the reaction of (V) with sulphur, (VI) and the saturated cyclic sulphides being unaffected, then spectroscopic analysis of (i) indicates 37% of (V) and 23% of (VI); thus of the 0.60 mol. of (V) present in the original cyclic sulphide 0.33 mol. is unaffected, 0.16 mol. is isomerised to (VI), and 0.12 mol. is converted into polysulphide.

Reaction of Diene (I)—Cyclic Sulphide with Sulphur.—The cyclic sulphide had $n_{\text{D}}^{20} 1.4920$

(Found: C, 70.3; H, 10.85; S, 18.3%), $E_{1\text{cm}}^{1\%}$ 38 at 2290 Å, and contained 45% of (V), >7% of (VI), and the saturated cyclic sulphides (III) and (IV) [(III > (IV)], but no triene (II). The cyclic sulphide (3.0 g.) and sulphur (0.3 g.) were heated *in vacuo* at 140° for 48 hr. Fractionation of the product gave: (i) cyclic sulphide (1.67 g.), b. p. 90—95°/10 mm., n_D^{20} 1.4937 (Found: C, 70.2; H, 11.2; S, 18.65%), $E_{1\text{cm}}^{1\%}$ 268 at 2290 Å in EtOH, containing 59% of (VI) and ~30—40% of (III), but no (V); and (ii) a polysulphide, b. p. <140°/0.01 mm., n_D^{20} 1.5691 (1.3 g.) [Found: C, 57.5; H, 8.85; S, 34.0%; M , 385. Corresponds to $(C_{10}H_{18.3}S_{2.2})_{1.84}$]. The polysulphide was predominantly saturated. The presence of cross-linked structures based on the mercaptocyclic sulphides (XVII)—(XIX) is indicated by the infrared spectrum, although this does not resemble (XVII) or (XVIII) sufficiently closely to indicate whether the polysulphide has primary and/or tertiary C—S cross-links. However, the presence of a *gem*-dimethyl group, indicated by the splitting of the methyl deformation band, shows that some tertiary C—S groups must be present.

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