

*The Reactions of Amines and Sulphur with Olefins. Part III.**
The Reaction of Diethylamine and Sulphur with 1:5-Diolefins.

By R. W. GLAZEBROOK and R. W. SAVILLE.

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2:6-Dimethylocta-2:6-diene (I) with the sulphur-diethylamine combination at 140° yields mainly saturated cross-linked sulphides, RS_xR , where R contains thiacyclopentane groups adjacent to the sulphide cross-link ($x = 1$ or 2), together with the cyclic sulphides (II) and (VI)—(VIII), formed by intramolecular sulphuration of (I). Infra-red spectroscopic evidence suggests the occurrence of similar cyclic structures in squalene polysulphide and in ebonite.

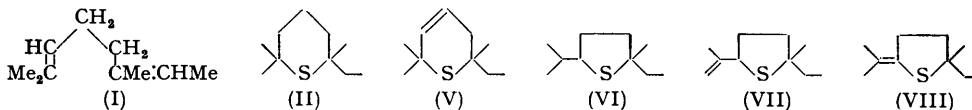
FARMER and SHIPLEY (*J.*, 1947, 1519) first showed that the action of sulphur on 2:6-dimethylocta-2:6-diene (I) at 140° gives both a cyclic monosulphide formed by intramolecular sulphuration of the diolefin and an approximately equal proportion of a cross-linked polysulphide, RS_xR' , which appeared to be analogous to the products obtained from sulphur and mono-olefins. Similar studies of the normal addition of hydrogen sulphide to (I) (Naylor, *J.*, 1947, 1532) showed that negligible cross-linked material is formed, the main product being 2-ethyl-2:6:6-trimethylthiacyclohexane (II), together with smaller amounts of the intermediate monothiols (III) and (IV) (see p. 2096). Farmer and Shipley (*loc. cit.*) did not determine the detailed structures of their cyclic monosulphide fraction, the heterogeneity of which was to be expected in view of the numerous possible reaction courses by which the sulphuration reaction could proceed. However, infra-red analysis of their product revealed vinylidene unsaturation, $CH_2:CRR'$, and the apparent presence of 6-ethyl-2:2:6-trimethylthiacyclohex-3-ene (V) as judged by comparison with (II) (Naylor, *loc. cit.*).

A logical extension of the work described in Parts I and II to determine the influence of amines on the structural pattern of the sulphur linkage in rubber-sulphur vulcanisates was to study the reaction of diethylamine and sulphur with (I) at 140°. The major

* Part I, *J.*, 1954, 2082. Part II, preceding paper.

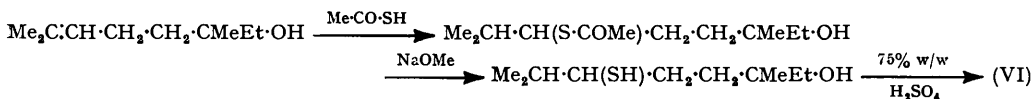
products proved to be (1) a cyclic sulphide fraction and (2) a cross-linked polysulphide, in the approximate ratio of 1 : 2.

Constitution of the Cyclic Sulphide Fraction (1).—Infra-red analysis revealed the presence of (II), and of 2-ethyl-2-methyl-5-isopropylthiacyclopentane (VI), but (V) appeared to be absent, as judged by the failure to detect unsaturation of the type *cis*-R·CH:CH·R', and by comparison of the infra-red spectrum of (1) with that of the analogous 2 : 2 : 6 : 6-tetra-methylthiacyclohex-3-ene (Naylor, *J.*, 1949, 2749). The spectrum further revealed the presence of ~20% vinylidene unsaturation, CH₂:CRR', and the absence of all other types

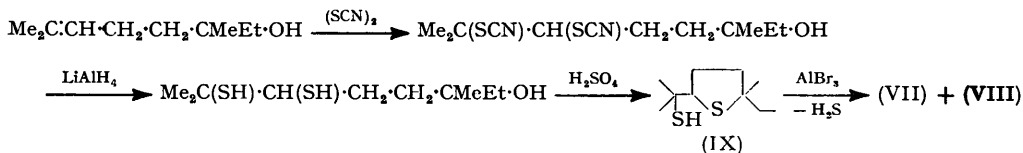


of double bond. Subsequent behaviour on hydrogenation, however, indicated that further unsaturation must be present and, in fact, the ultra-violet absorption at ~2300 Å indicated the presence of the vinyl sulphide grouping C=C-S. It seemed highly probable that the latter was present as a tetrasubstituted double bond CRR':CR''SR'', undetectable in the infra-red region, and that the above types of unsaturation were associated with the thiacyclopentane structures (VII) and (VIII), respectively. This view was confirmed when catalytic hydrogenation of the cyclic sulphide fraction resulted in an increased proportion of (VI), while the amount of (II) present remained constant. Further, a sample of (1) which contained solely unsaturation of the type CRR':CR''SR'' and was free from the saturated sulphides (II) and (VI), gave on catalytic hydrogenation, pure (VI).

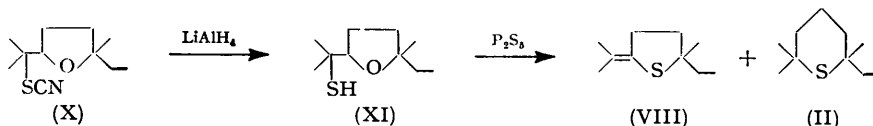
Synthesis of Cyclic Sulphides.—The spectroscopic work necessitated synthesis of the cyclic sulphides (II), (VI), (VII), and (VIII). The first was prepared by the normal addition of hydrogen sulphide to (I), catalysed by 75% w/w sulphuric acid or aluminium bromide (cf. Arnold, B.P. 602,238; Van Riemsdijk, Van Stennis, and Waterman, *J. Inst. Petrol.*, 1951, 37, 265). The second sulphide (VI) was prepared by the route :



Synthesis of the unsaturated thiacyclopentanes (VII) and (VIII) presented considerable difficulties and only partial success was achieved by the proposed route :



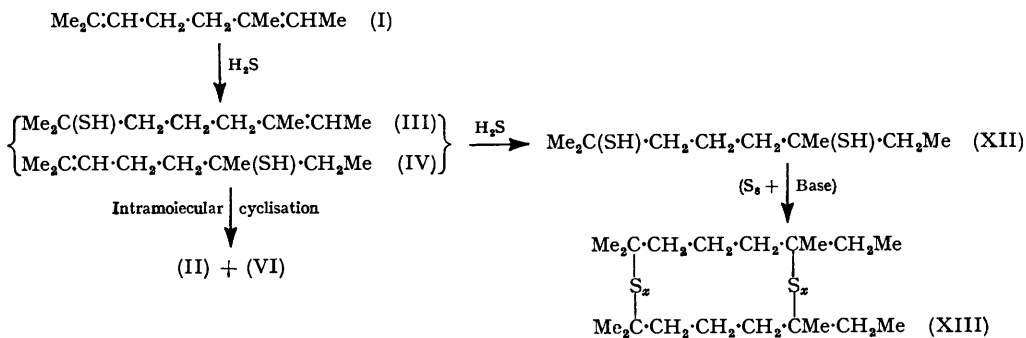
Addition of dithiocyanogen to 3 : 7-dimethyloct-6-en-3-ol (cf. Wood, "Organic Reactions," Wiley, New York, 1946, Vol. III, p. 240) resulted unexpectedly in the immediate cyclisation of the dithiocyanato-adduct to give the cyclic ether (X). Reduction of the latter



with lithium aluminium hydride (Backer and Strating, *Rec. Trav. chim.*, 1950, 69, 638) gave a high yield of 2-ethyl-2 : 3 : 4 : 5-tetrahydro-5-(1-mercapto-1-methylethyl)-2-methylfuran (XI). Attempted replacement of the oxygen in (XI) by sulphur by reaction with phosphorus pentasulphide (Naylor, *J.*, 1947, 1106) led unexpectedly to a product containing neither thiol groups nor vinylidene unsaturation; it was mainly a mixture of (II) and

(VIII), the latter being probably formed by cleavage of the *tert.*-C-S bond in (XI) with elimination of hydrogen sulphide. Comparison of the infra-red spectrum of this product with that obtained from the reaction of (I) with diethylamine and sulphur revealed similarities. Cyclisation of the dithiocyanato-adduct to give the *six*-membered cyclic ether analogous to (X) appeared unlikely, as judged by the dissimilarity of the infra-red spectrum of the derived mercaptocyclic ether (XI) from those of known tetrahydropyrans (Naylor, *loc. cit.*); and stronger evidence for this view was provided by the fact that thiol elimination from a tetrahydromercaptopyran analogous to (XI) would have yielded (V), which was not present in the product. It seemed probable that (II) arose by ring-expansion during the reaction of (XI) with phosphorus pentasulphide, since Birch (*J. Inst. Petrol.*, 1953, **39**, 195) found that the high-temperature reaction of tetrahydrofurfuryl alcohol with hydrogen sulphide and alumina yields a mixture of thiacyclohex-2-ene and thiacyclohexane.

Constitution of the Cross-linked Polysulphide Fraction (2).—Elementary analysis and molecular-weight determination showed that fraction (2) consisted of two di-isoprene molecules for every 3 or 4 sulphur atoms, and infra-red analysis revealed that it was largely saturated and thiol-free. On this basis, it appeared initially that (2) consisted mainly of the polysulphide (XIII) formed by base-catalysed sulphur oxidation of the intermediate dithiol (XII), the latter resulting from addition of two molecules of hydrogen sulphide (formed by prior reaction of diethylamine with sulphur) to (I):

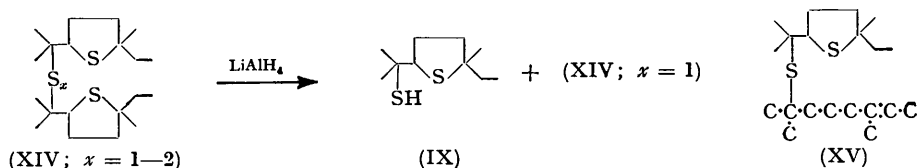


This apparently simple reaction course was subsequently shown to be invalid by the synthetic and degradative methods described below.

The dithiol (XII) was synthesised by the addition of toluene- ω -thiol to 3:7-dimethyloct-6-en-3-ol in the presence of 75% w/w sulphuric acid, followed by reductive cleavage of the resulting dibenzylthio-compound with sodium in liquid ammonia. This method considerably reduced the competing cyclisation of the diolefin encountered when (I) was used directly. Base-catalysed oxidation of (XII) with sulphur gave a saturated, thiol-free polysulphide of the type (XIII), or possibly of the polymeric chain type $\text{R}\cdot\text{S}_x\cdot\text{R}'\cdot\text{S}_x\cdot\text{R}'\cdot\text{S}_x\cdot\text{R}$, which had, however, a quite distinct infra-red spectrum from that of fraction (2).

Hydrogenolysis of the cross-linked polysulphide (2) with lithium aluminium hydride (Arnold, Lien, and Alm, *J. Amer. Chem. Soc.*, 1950, **72**, 731) gave (3) a high yield of an essentially saturated thiol $\text{C}_{10}\text{H}_{20}\text{S}_2$, and (4) a thiol-free product $\text{C}_{20}\text{H}_{38}\text{S}_{2-3}$. No hydrogen sulphide was formed during the hydrogenolysis, indicating that (2) was devoid of polysulphidic sulphur. The thiol value of (3) showed that only half the sulphur was present as a thiol group, and the low molecular weight (204) ruled out any possibility of a cross-linked structure containing two di-isoprene units. The remaining sulphur must therefore be present in cyclic sulphide form and, in fact, the infra-red spectrum of (3) was similar to that of the cyclic sulphide fraction (1), except for the presence of thiol groups and the absence of unsaturation. The structure of (3) as the mercaptothiacyclopentane (IX) was finally established by the close identity of its infra-red spectrum with that of authentic (IX) obtained by addition of thiolacetic acid to (VIII) and subsequent hydrolysis of the acetyl-

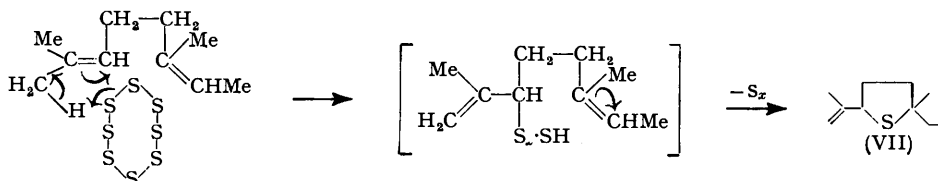
thio-derivative. This leads to the view that the parent cross-linked polysulphide (2) consists mainly of the structures represented by (XIV) in which the cross-link is predominantly mono- and di-sulphidic. On this basis part of (2) should remain unaffected



by the hydrogenolysis and, in fact, infra-red examination of the thiol-free product (4) showed that it was closely similar to the original cross-linked polysulphide (2), and to (IX) except for the absence of a band due to the thiol group in the latter, and it must therefore be mainly (XIV; $x = 1$). The presence of a small amount of trialkylethylene unsaturation in (4) is attributed to the presence of minor amounts of structures such as (XV) formed by addition of (IX) to (I); the elementary analysis and intensity of the infra-red band due to $\text{RR}'\text{C}:\text{CHR}''$ are suggestive of (XIV; $x = 1$) and (XV) being present in (4) in the ratio of 4 : 1.

The structure (XIV) is clearly consistent with the mono- and di-sulphide cross-linked products obtained from the mono-olefins (Parts I and II). The isolation of *tert.*-alkane-thiols from trialkylethylenes (Part II) led to a closer search for (IX) in the present reaction, and its presence was established in a small intermediate fraction between the main products (1) and (2).

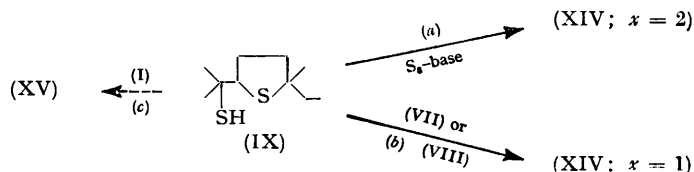
Reaction Mechanism.—A primary process in the sulphuration of (I) with the diethylamine-sulphur combination undoubtedly involves polar addition of hydrogen sulphide, formed by prior interaction of the diethylamine and sulphur, to (I). Polar cyclisation of the resulting *tert.*-thiols (III) and (IV) then gives the substituted thiacyclohexane (II). To account for the substituted thiacyclopentane (VII) and the main cross-linked product (XIV; $x = 1-2$) by a polar mechanism, it is necessary to envisage an electrophilic attack by sulphur at the unmethylated end of a double bond in (I) (cf. Van Veersen, *Rubber Chem. Tech.*, 1951, **24**, 169), followed by cyclisation of an intermediate mercapto-compound as suggested by :



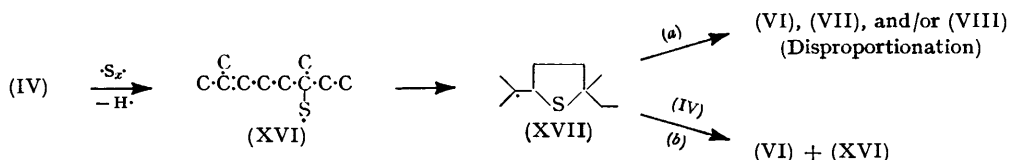
The analogous intermediate formed by the comparable attack of sulphur at the alternative double bond in (I) is unlikely to cyclise, since a seven-membered ring would result. Subsequent polar addition of hydrogen sulphide to (VII) yields (IX), and the latter undergoes (a) base-catalysed sulphur oxidation to give the major cross-linked polysulphide product (XIV; $x = 2$), (b) polar addition to the unsaturated cyclic sulphides (VII) or (VIII) to give (XIV; $x = 1$), or (c) polar addition to (I) to give (XV). In the presence of diethylamine, preferential oxidation of (IX) by path (a) will undoubtedly reduce $\text{RR}'\text{C}:\text{CHR}''$ unsaturation due to (XV) in the cross-linked product; (XV) is more likely to be obtained in higher proportion in sulphurations conducted in the absence of amine. A further important finding was that (VII) when heated with a catalytic amount of sulphur at 140° isomerises to (VIII), and this reaction may be responsible for the formation of (VIII) in the above experiments. Comparable isomerisations of allylic to vinylic sulphides have been effected by Tarbell and McCall (*J. Amer. Chem. Soc.*, 1952, **74**, 48).

The polar mechanism depicted above offers a self-consistent picture for the formation of most of the identified products and is in accordance with the reaction characteristics observed in the sulphuration of mono-olefins described in Parts I and II. The direct

combination of sulphur is supported by the virtual absence of cross-linked sulphides in the reaction of hydrogen sulphide with (I) (Naylor, *J.*, 1947, 1532) where sulphur is not available for the above type of attack. No adequate explanation can be offered for the formation of the saturated thiacyclopentane (VI) by a polar mechanism, and thus one is forced to the view that free-radical sulphuration processes must participate to some extent. The co-existence of polar and free-radical mechanisms, capable of being influenced by small

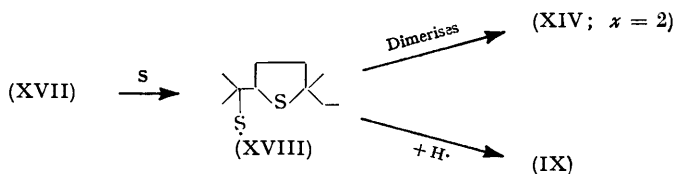


changes in experimental conditions, has been recognised by various workers (see Salomon, *Discuss. Faraday Soc.*, 1947, 2, 353). The formation of (VI) can be explained by abnormal cyclisation of the open-chain alkylthio-radical (XVI), formed by loss of a hydrogen atom from the thiol (IV) on oxidation with sulphur. The resulting cyclic radical (XVII) may then be stabilised (a) by disproportionation to (VI) and (VII) or (VIII), or (b) by hydrogen-atom capture from the thiol (IV) :



Naylor (*loc. cit.*) noted the reluctance of the thiol (IV) or (III) to cyclise by a polar mechanism to give (II) in the sulphur- or aluminium sulphide-catalysed addition of hydrogen sulphide to (I). Repetition of these experiments has now shown that the five-membered ring (VI) is also formed, possibly by the preferential cyclisation of (IV) in the above manner.

Free-radical attack of sulphur on (XVII) may also occur to a minor extent to give (XVIII), which may then dimerise to give (XIV; $x = 2$) or capture a hydrogen atom to give (IX) :



It remains for future work to determine the relative importance of polar and free-radical mechanisms in sulphuration reactions of the present type.

Sulphuration of Polyisoprenes.—Many synthetic dialkyl tetrasulphides when boiled with sodium sulphite solution lose half their sulphur content, forming disulphides (Farmer and Shipley, *J.*, 1947, 1519; Bloomfield, *J.*, 1947, 1547), and Armstrong, Little, and Doak (*Ind. Eng. Chem.*, 1944, 36, 628) showed that the polysulphide from sulphur and 2-methylbut-2-ene behaves likewise. On the other hand, Farmer, Shipley, and Bloomfield (*loc. cit.*) observed negligible removal of combined sulphur from the polysulphides of dihydro-myrcene, geraniolene, and squalene. Such behaviour is to be expected if it is assumed that the latter possess only 1—2 sulphur atoms in the cross-link and the remainder in cyclic sulphide form, in contrast to the dialkyl polysulphides containing linear cross-links of more than 2 sulphur atoms. These considerations suggested that cyclic structures of the present type may be obtained from olefins containing more than 2 isoprene units, and therefore squalene polysulphide and ebonite were examined. The choice of ebonite in preference to soft-vulcanised rubber was made for two reasons: (a) For the identification of the cyclic sulphide

structures by infra-red methods, the material must contain about 30% of combined sulphur; and (b) for a true comparison with (XIV) the material must possess little residual unsaturation. Thus, although the use of infra-red analysis for the examination of conventional vulcanisates is very limited, these requirements are fulfilled by ebonite. The spectrum of (XIV) was compared with those of squalene polysulphide and ebonite, and distinct similarities were observed, notably a band of quite similar shape and intensity at 945 cm.^{-1} in (XIV), 953 cm.^{-1} in squalene polysulphide, and 947 cm.^{-1} in ebonite, which was not present in the pure hydrocarbons. This band cannot be due, as believed by Sheppard and Sutherland (*J.*, 1947, 1699), to *trans*-RCH:CHR, which always occurs close to 965 cm.^{-1} in allylic sulphides, but rather suggests the presence of cyclic structures of type (VI) in the above materials.

EXPERIMENTAL

Infra-red spectra were recorded on a Grubb-Parsons single-beam spectrometer. Ultra-violet light absorption measurements were made with absolute ethanol solutions by means of a Hilger Uvispek photoelectric spectrophotometer. Microanalyses were conducted under the supervision of Dr. W. T. Chambers.

2 : 6-Dimethylocta-2 : 6-diene (I).—This was prepared by reduction of purified geraniol with sodium and liquid ammonia; b. p. $56.0^\circ/14\text{ mm.}$, $n_D^{20} 1.4520$ (Found : C, 86.85; H, 12.8. Calc. for $C_{10}H_{18}$: C, 87.0; H, 13.0%). Infra-red analysis revealed the absence of hydroxyl groups and less than 1% of vinylidene unsaturation, $CH_2=CRR'$. (I) was unchanged after 24 hours' heating at 140° with diethylamine or phenylhydrazine.

Synthesis of 2-Ethyl-2-methyl-5-isopropylthiacyclopentane (VI).—3 : 7-Dimethyloct-6-en-3-ol. Reaction of the Grignard reagent (25% excess) from magnesium (24 g.) and ethyl bromide (109 g.) with 6-methylhept-5-en-2-one (100 g.; b. p. $58-59^\circ/10\text{ mm.}$, $n_D^{20} 1.4420$) in the usual manner gave the *tert.*-alcohol, b. p. $87^\circ/12\text{ mm.}$, $n_D^{20} 1.4548$ (108 g.) (Found : C, 76.7; H, 13.0. Calc. for $C_{10}H_{20}O$: C, 76.9; H, 12.8%).

4-Hydroxy-4-methyl-1-isopropylhexyl thiolacetate. The above *tert.*-alcohol (25 g.) reacted exothermally with freshly distilled thioacetic acid (14 g.). After the initial reaction had subsided, the liquid was warmed on the steam-bath for 30 min. Distillation yielded the *thiolacetate*, b. p. $110-111^\circ/0.01\text{ mm.}$ (34 g., 92%), $n_D^{20} 1.4848$ (Found : C, 61.9; H, 10.3; S, 13.8. $C_{12}H_{24}O_2S$ requires C, 62.0; H, 10.3; S, 13.8%).

3-Mercapto-2 : 6-dimethyloctan-6-ol. The thiolacetate (33 g.) was hydrolysed overnight in methanol (500 ml.) containing a trace of sodium methoxide. After removal of most of the solvent by distillation, water was added, and the liquid extracted with ether. Distillation gave the *hydroxy-thiol* (20 g., 73%), b. p. $61-62^\circ/0.01\text{ mm.}$, $n_D^{20} 1.4800$ (Found : C, 62.9; H, 11.35; S, 16.9; SH, 17.4. $C_{10}H_{22}OS$ requires C, 63.2; H, 11.6; S, 16.85; SH, 17.4%). This (20 g.) was added slowly, with stirring, to 75% w/w sulphuric acid (100 g.) at 0° . The mixture was then allowed to reach room temperature and stirred for 15 min. Ice and water were added and the *thiacyclopentane* (VI) was isolated in the usual manner, b. p. $87^\circ/10\text{ mm.}$ (14 g., 77%), $n_D^{20} 1.4765$ (Found : C, 69.6; H, 11.5; S, 18.9. $C_{10}H_{20}S$ requires C, 69.8; H, 11.6; S, 18.6%) : with chloramine-r it formed a *sulphidimine*, needles (from aqueous methanol), m. p. 135° (Found : C, 59.6; H, 8.1; N, 4.2; S, 18.4. $C_{17}H_{27}O_2NS_2$ requires C, 59.8; H, 7.9; N, 4.1; S, 18.8%), which depressed the m. p. of toluene-*p*-sulphonamide. Reaction of (VI) with peracetic acid in the usual manner gave a liquid *sulphone*, b. p. $88^\circ/0.001\text{ mm.}$, $n_D^{20} 1.4771$ (Found : C, 59.0; H, 10.1; S, 15.6. $C_{10}H_{20}O_2S$ requires C, 58.9; H, 9.8; S, 15.7%).

Addition of Dithiocyanogen to 3 : 7-Dimethyloct-6-en-3-ol.—Lead thiocyanate (36 g., 0.11 mol.) in dry chloroform (130 ml.) was cooled to $5-10^\circ$, and bromine (16 g., 0.1 mol.) in chloroform (50 ml.) added with vigorous stirring. The chloroform was decanted, and the residual solid washed with more solvent. The combined solutions were mixed with the *tert.*-alcohol (12.0 g., 0.08 mol.) in chloroform (20 ml.) at 10° , and kept overnight at room temperature. The yellow precipitate of polythiocyanogen was filtered off, and the chloroform solution diluted with ether, washed (water, thiosulphate, water), dried (Na_2SO_4), and fractionated. The 2-ethyl-2 : 3 : 4 : 5-tetrahydro-2-methyl-5-(1-methyl-1-thiocyanatoethyl)furan had b. p. $62^\circ/0.05\text{ mm.}$, $n_D^{20} 1.4880$ (7.5 g.) (Found : C, 61.85; H, 8.8; N, 6.7. $C_{11}H_{19}ONS$ requires C, 61.9; H, 8.9; N, 6.6%). The infra-red spectrum showed the absence of hydroxyl groups and unsaturation, but a band at 2160 cm.^{-1} clearly indicated SCN. The remainder of the spectrum was consistent with the cyclic ether structure (X).

Use of phenyl iododichloride for the thiocyanation (cf. Neu, *Ber.*, 1939, 72, 1505)

gave a light yellow liquid, b. p. $80^{\circ}/0.08$ mm., n_D^{20} 1.4870 (Found: C, 60.7; H, 8.65; N, 6.5%). The spectra of the two products were almost identical.

Reduction of (X).—This compound (3.4 g.) was added dropwise with vigorous stirring to lithium aluminium hydride (0.90 g., 2 equiv.) in dry ether (40 ml.). After refluxing for 15 min., the liquid was decomposed with ice and dilute sulphuric acid, and the usual method of isolation gave 2-ethyl-2 : 3 : 4 : 5-tetrahydro-5-(1-mercapto-1-methylethyl)-2-methylfuran (XI), b. p. $88^{\circ}/10$ mm., n_D^{20} 1.4740 (2.8 g., 93%) (Found: C, 64.0; H, 10.65; S, 16.8; N, 0.2; SH, 17.6. $C_{10}H_{20}OS$ requires C, 63.8; H, 10.6; S, 17.0; SH, 17.5%). The spectrum of this colourless liquid was very similar to that of the original thiocyanato-compound (X) except for the replacement of the SCN band by that of SH at 2570 cm^{-1} . Hydroxyl groups and unsaturation were again absent, and Rheinboldt's test indicated that (XI) was a *tert.*-thiol.

Action of Phosphorus Pentasulphide on (XI).—This compound (4.5 g.) and phosphorus pentasulphide (8.0 g.) were heated at $<10^{-3}$ mm. in a Carius tube for 6 hr. at 110° . The product was extracted repeatedly with ether and mixed with water, and the aqueous solution extracted. After drying, fractionation gave a liquid, b. p. $80^{\circ}/12$ mm., n_D^{20} 1.4922 (1.3 g.) (Found: C, 70.2; H, 11.0; S, 18.7. Calc. for $C_{10}H_{20}S$: C, 69.8; H, 11.6; S, 18.6. Calc. for $C_{10}H_{18}S$: C, 70.5; H, 10.65; S, 18.85%). Infra-red analysis revealed that thiol groups and vinylidene unsaturation $CH_2=CRR'$ were absent. Light absorption: max. 2275 Å; ϵ 1830 (for M , 170). The spectra were consistent with a mixture of (II) and (VIII), though $>25\%$ of $C=C-S$ grouping, due to the latter, was present. The cyclic sulphides (V) and (VI) were absent from this product, but comparison of the spectrum with that of the cyclic sulphide fraction (I) from the reaction of sulphur-diethylamine with (I) revealed definite similarities.

2 : 6-Dibenzylthio-2 : 6-dimethyloctane.—3 : 7-Dimethyloct-6-en-3-ol (15.6 g., 0.1 mol.) was stirred vigorously at $0-5^{\circ}$ with toluene- ω -thiol (24.8 g., 2 mol.) while sulphuric acid (100 g., 75% w/w) was added slowly (1 hr.). After a further hour's stirring at room temperature, decomposition with ice and the usual method of working up gave unchanged thiol (5.0 g.) and the dibenzylthio-compound, a colourless short-path distillate, n_D^{20} 1.5670 (10.9 g.) (Found: C, 74.5; H, 8.75; S, 17.0. $C_{24}H_{34}S_2$ requires C, 74.6; H, 8.8; S, 16.6%). The infra-red spectrum confirmed the absence of hydroxyl and thiol groups and also of olefinic unsaturation.

2 : 6-Dimercapto-2 : 6-dimethyloctane (XII).—The above dibenzylthio-compound (7.7 g., 0.02 mol.) in liquid ammonia (200 ml.) was cleaved with sodium (2.0 g., 1.1 equiv.) in the usual manner. After decomposition with ammonium chloride, the dithiol isolated had b. p. $119^{\circ}/15$ mm. (3.7 g., 90%), n_D^{20} 1.5017 (Found: C, 62.1; H, 10.35; S, 27.6. $C_{10}H_{22}S_2$ requires C, 58.3; H, 10.7; S, 31.0%). Rheinboldt's test indicated a tertiary thiol, and copper butyl phthalate estimation gave SH, 30.0 ($C_{10}H_{22}S_2$ requires SH, 32.0%). The infra-red spectrum revealed traces of the original dibenzylthio-compound as impurity, but refractionation gave a purer sample of the dithiol (XII), b. p. $112^{\circ}/10$ mm. (Found: C, 58.65; H, 10.4; S, 30.2%). No unsaturation could be detected.

Oxidative Cross-linking of (XII).—This dithiol (1.90 g.) was mixed with sulphur (0.2 g.) and diethylamine (0.1 g.). The polysulphide was isolated in the usual manner and purified by chromatography on silica gel. The spectrum bore no resemblance to that of the polysulphide (XIV) obtained from reaction of sulphur-diethylamine with (I).

Addition of Hydrogen Sulphide to (I).—(a) Hydrogen sulphide was passed rapidly into (I) (15 g.) in 75% w/w sulphuric acid (100 g.) at 0° with stirring during 4 hr. After addition of ice, the product isolated contained thiol (SH, 6.6%). Removal of the latter with copper butyl phthalate and fractionation gave (II), b. p. $81-82^{\circ}/10$ mm., n_D^{20} 1.4857 (Found: C, 70.0; H, 11.8; S, 18.3. Calc. for $C_{10}H_{20}S$: C, 69.8; H, 11.6; S, 18.6%). The yield was never $>10\%$ owing to the cyclisation of (I).

(b) A rapid stream of dry, purified hydrogen sulphide was passed into a solution of freshly sublimed aluminium bromide (2.0 g.) in carbon disulphide (50 ml.) while (I) (20 ml.) was simultaneously added during 1 hr. Fractionation of the isolated product gave: (i) b. p. $70^{\circ}/12$ mm. (6.1 g.), n_D^{20} 1.4772 (Found: C, 75.7; H, 12.5; S, 12.1%); (ii) b. p. $70-80^{\circ}/12$ mm. (4.5 g.), n_D^{20} 1.4880 (Found: C, 69.4; H, 11.65; S, 18.6. Calc. for $C_{10}H_{20}S$: C, 69.8; H, 11.6; S, 18.6%); (iii) b. p. $80-120^{\circ}/12$ mm. (3.0 g.), n_D^{20} 1.4922 (Found: C, 68.3; H, 11.65; S, 19.35%); (iv) b. p. $120^{\circ}/12$ mm. (1.90 g.), n_D^{20} 1.4950 (Found: C, 62.1; H, 10.95; S, 25.6%). The infra-red spectra revealed that all the fractions were saturated; the main constituent of (i)–(iii) was (II), with the dithiol (XII) in minor amount, fractionation failing to effect complete separation. The intensity of the SH band in (iv) indicated that the dithiol was the major constituent (Found: SH, 24.8. Calc. for $C_{10}H_{22}S_2$: SH, 31.0%).

Action of Sulphur on (I) in the Presence of Diethylamine.—The diene (I) (50.0 g.) and diethyl-

amine (30.0 g.) were heated with sulphur (10.0 g.) at $<10^{-3}$ mm. in a Carius tube for 20 hr. at $140^\circ \pm 1^\circ$. The resulting dark brown liquid, which contained no tar and negligible amine hydrogen sulphide, was washed out with ligroin, and material of low b. p. removed on the steam-bath in nitrogen. Fractionation of the residue gave unchanged (I) (25.1 g.), b. p. 68—84°/20 mm., n_D^{20} 1.4530, containing a trace of sulphide (Found: S, 1.43%), and the products in three main fractions: (i) b. p. 84—96°/20 mm. (8.3 g.), n_D^{20} 1.4920 (Found: C, 70.7; H, 11.15; N, 0.8; S, 16.95. 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%); (ii) b. p. 48—65°/0.03 mm. (12.1 g.), n_D^{20} 1.5300; and (iii) a final residue, not distillable below 140°/0.03 mm. (18.0 g.). The infra-red spectrum of the recovered olefin showed negligible $CH_2:CRR'$ unsaturation, indicating the absence of appreciable isomerisation or cyclisation.

Infra-red analysis of the cyclic sulphide fraction (i) indicated ~20% of $CH_2:CRR'$ groups due to (VII) and only traces of *N*-ethylthioacetamide and (I). Negligible trialkylethylene unsaturation was detected and the absence of (V) was confirmed by comparison with the spectrum of the analogous 2:2:6:6-tetramethylthiacyclohex-3-ene. The presence of the saturated cyclic sulphides (II) and (VI) was confirmed, while the ultra-violet spectrum indicated ~40% of $C=C-S$ grouping due to (VIII) in this fraction (i). Thiol groups were absent. Mercuric chloride gave a white, solid derivative insoluble in all common solvents.

Addition of ligroin to (ii) precipitated an orange-red layer, b. p. 54—62°/0.1 mm. (3.1 g.), n_D^{20} 1.5450 (Found: C, 52.9; H, 9.55; N, 10.3%). The spectrum and chemical reactions indicated mainly *N*-ethylthioacetamide, negligible olefin sulphides being detectable. The main ligroin solution from (ii) was extracted with 50% hydrochloric acid (4 × 25 ml.), dried, and distilled, giving: (a) b. p. 40°/0.1 mm. (1.85 g.), n_D^{20} 1.5000 (Found: C, 68.5; H, 10.6; N, 0.06; S, 20.8%); (b) b. p. 50—60°/0.1 mm. (2.4 g.), n_D^{20} 1.5172 (Found: C, 64.05; H, 10.0; N, 0.17; S, 25.7; SH, 7.0%); and (c) b. p. 60—65°/0.1 mm. (1.2 g.), n_D^{20} 1.5270 [Found: C, 60.2; H, 9.6; N, 0.47; S, 30.35; SH, 9.0%; *M* (ebullioscopic in benzene), 190]. The thiol values of (b) and (c) were determined argentometrically as copper butyl phthalate titration gave indefinite end-points; Rheinboldt's test indicated tertiary thiol in both cases. Infra-red analysis revealed negligible $CH_2:CRR'$ groups and <10% of trialkylethylene-type unsaturation. The fractions were otherwise saturated, containing a large proportion of the cyclic thiol-sulphide (IX) (Calc. for $C_{10}H_{20}S_2$: C, 58.8; H, 9.8; S, 31.4; SH, 16.2%; *M*, 204). The thiol value of (c) indicated 56% of (IX) and infra-red analysis gave ~60%.

The final residue (iii) (18.0 g.) was dissolved in excess of ligroin and extracted with 50% hydrochloric acid (4 × 25 ml.) and further purified by chromatography on silica gel; ~95% of the resulting clear, yellow oil distilled at 120—140° in a short-path still, two typical fractions only being recorded: (a) n_D^{20} 1.5312 [Found: C, 63.15; H, 10.0; S, 26.8%; *M* (ebullioscopic in benzene), 310]; and (b) n_D^{20} 1.5395 (Found: C, 62.75; H, 10.0; S, 27.4%; *M*, 405). Infra-red analysis showed that the major product was thiol-free and saturated; bands at 1670 cm^{-1} and 827 cm^{-1} indicated 7—10% of $RCH:CR'R''$ (two $RCH:CR'R''$ groups per mol.). A small proportion (~12%) of $C=C-S$ was, however, present (light absorption: max. 2350 Å; ϵ 940), indicative of tetrasubstituted double bonds.

A further reaction for 6 hr. at $140^\circ \pm 1^\circ$ with sulphur (5.0 g.), diethylamine (15.0 g.), and (I) (40.0 g.) gave the cyclic sulphide fraction (7.5 g.) containing thioamides, which on acid extraction and fractionation gave: (i) b. p. 88—94°/15 mm. (2.9 g.), n_D^{20} 1.4961 [Found: C, 71.55; H, 10.85; N, 0; S, 16.65; *M* (ebullioscopic in benzene), 156, 159]; and (ii) b. p. 100—125°/15 mm. (2.94 g.), n_D^{20} 1.5155 (Found: C, 65.85; H, 9.65; N, 0.54; S, 22.6%; *M*, 178, 181). A trace of the di-isoprene (I) was present in (i). A band at 890 cm^{-1} due to $CH_2:CRR'$ groups in the infra-red spectra of (i) and (ii) suggested that more of (VII) was obtained in this shorter reaction period, the amount of (VII) in (i) and (ii) being 40% and 30% respectively. The saturated ring (II) was present in both fractions, but neither (V) nor (VI) was detectable. Ultra-violet examination was not carried out in this experiment. The polysulphide residue (8.1 g.) was purified by chromatography on alumina (Found: C, 59.55; H, 9.9; N, 0.11; S, 30.5. Calc. for $C_{20}H_{38}S_4$: C, 59.1; H, 9.4; S, 31.5%). The presence of only mono- and di-sulphide cross-links in this material (cf. XIV) was confirmed by sulphite treatment. Thus, the total sulphur loss (cf. Farmer and Shipley, *loc. cit.*) was 1.4% (5 hr. at 100°, using 10% sodium sulphite solution).

Reactions of the Cyclic Sulphide Fraction (i).—(a) *Hydrogenation.* The sample used had b. p. 85—90°/10 mm., n_D^{20} 1.4887 (Found: C, 70.5; H, 11.35; S, 18.2%; C:H, 10:19.3). Infra-red analysis revealed 15% of $CH_2:CRR'$. The sample (3.04 g.), when hydrogenated over palladium on charcoal (Bateman and Shipley, forthcoming publication), absorbed 240 ml. of

hydrogen (N.T.P.); unsaturation, 60%/mol. The product, b. p. 85—87°/10 mm., n_D^{20} 1.4800 (Found: C, 70.0; H, 11.65; S, 18.4. Calc. for $C_{10}H_{20}S$: C, 69.8; H, 11.6; S, 18.6%), contained no thiol, but infra-red analysis showed that it consisted of (II) and (VI); the amount of the former had remained constant but that of the latter had increased. A second sample of cyclic sulphide, free from (II) and (VI) by fractional elution from silica gel and shown by infra-red analysis to contain only $CRR':CR''SR''$ -type unsaturation due to (VIII), was similarly hydrogenated. The theoretical amount of hydrogen was absorbed (one double bond per molecule), and infra-red analysis of the product revealed pure (VI).

(b) *Reaction with thiolacetic acid.*—The cyclic sulphide sample used contained both (II) and (VI) but the unsaturation was almost entirely due to (VIII), being of the tetrasubstituted type. Freshly distilled thiolacetic acid (10.0 g.) and the cyclic sulphide sample (15.0 g.) were irradiated with ultra-violet light for 7 hr. at 15°. Distillation yielded: (i) unchanged acid (9.0 g.), b. p. 85—90°/760 mm.; (ii) saturated cyclic sulphide, b. p. 80—90°/10 mm. (12.0 g.), shown by infra-red analysis to be a mixture of (II) and (VI) unaffected by irradiation; and (iii) the thiolacetate, b. p. 73—77°/0.01 mm. (3.1 g.). Hydrolysis of the ester with aqueous-ethanolic potassium hydroxide under nitrogen gave *2-ethyl-5-(1-mercapto-1-methyl-ethyl)-2-methylthiacyclopentane* (IX), b. p. 48—50°/0.01 mm., n_D^{20} 1.5160 (Found: C, 58.8; H, 9.85; S, 31.0; SH, 16.1. $C_{10}H_{22}S_2$ requires C, 58.8; H, 9.8; S, 31.4; SH, 16.2%), presence of the five-membered ring being confirmed by comparison of the infra-red spectrum with that of (VI).

(c) *Isomerisation.* A sample of cyclic sulphide containing 14% of $CH_2:CRR'$ unsaturation due to (VII) was heated *in vacuo* with a catalytic amount of sulphur for 48 hr. at 140°. The infra-red spectrum of the product revealed 7% of $CH_2:CRR'$ unsaturation, no other appreciable change being detected. The ultra-violet spectrum indicated that ϵ_{2300} increased from ~1100 to ~1700 during the heating, the increase being due to 7% of $C=C-S$ chromophore. A blank experiment omitting sulphur confirmed the absence of purely thermal isomerisation of (VII) to (VIII).

In these experiments, the estimates of the $C=C-S$ grouping were based on the highest extinction coefficient with max. (ethanol) 2290 Å [ϵ 7750 was recorded for samples of (VIII) which contained no other type of unsaturation (cf. also Koch, *J.*, 1949, 387)].

Reactions of the Cross-linked Polysulphide Fraction (iii).—Hydrogenolysis. The main sulphide fraction (iii) from reaction of (I) with sulphur-diethylamine (20 hr. at 140°) was purified by chromatography on silica gel and by molecular distillation; it had n_D^{20} 1.5390 [Found: C, 62.7; H, 10.0; S, 27.6%; *M* (ebullioscopic in benzene), 400], corresponding to 2 olefin units per 3—4 sulphur atoms. The infra-red spectrum revealed 6—10% of $RCH:CR'R''$ groups (two $RCH:CR'R''$ groups/mole), and $CH_2:CRR'$ -type unsaturation was absent. Lithium aluminium hydride (1.50 g.) was stirred rapidly at room temperature with tetrahydrofuran (50 ml.) while (iii) (4.0 g.) was slowly added, the mixture then being refluxed for 4 hr. After decomposition with ice and 2*N*-sulphuric acid, two main fractions were isolated:

(a) B. p. 60—65°/0.5 mm. (55.0°/0.1 mm.) (2.4 g.), n_D^{20} 1.5168 [Found: C, 59.0; H, 10.0; S, 31.25; SH, 17.6%; *M* (ebullioscopic in benzene), 204. $C_{10}H_{20}S_2$ requires C, 58.8; H, 9.8; S, 31.4; SH, 16.2%; *M*, 204]. The *thiol* was largely saturated, the spectrum revealing <10% of $RCH:CR'R''$ (one C:C per *M* = 204). Comparison of the infra-red spectrum of (a) with those of (XII) and 3 : 7-dimercapto-2 : 6-dimethyloctane (Cunneen, *J.*, 1947, 139) confirmed that the latter two dithiols were absent. Comparison with the cyclic thiol-sulphide (IX) obtained from the reaction of thiolacetic acid with the cyclic sulphide fraction revealed that the two were almost identical. Excess of 10% mercuric cyanide with (a) in ethanol gave an oil which could not be crystallised, and aluminium bromide with (a) in benzene gave an immediate evolution of hydrogen sulphide.

Fraction (b) was a clear, yellow short-path distillate (1.30 g.), n_D^{20} 1.5185 [Found: C, 65.7; H, 10.6; S, 23.9; SH < 1%; *M* (ebullioscopic in benzene), 338]. The infra-red spectrum was practically identical with that of the cyclic thiol-sulphide (IX), apart from the SH band; $RCH:CR'R''$ type unsaturation (20%) probably due to (XV) was present [Calc. for $C_{20}H_{38}S_2$: C, 70.1; H, 11.1; S, 18.7. Calc. for $C_{20}H_{38}S_3$: C, 64.2; H, 10.2; S, 25.9. Calc. for (XIV; $\pi = 1$) and (XV) in the ratio 1 to 4: C, 65.5; H, 10.4; S, 23.5%].

The ultra-violet spectrum of the cleavage thiol (a) above showed little greater absorption than expected for a saturated sulphide with two sulphur atoms.

Squalene Polysulphide.—Squalene (13.0 g.), purified by molecular distillation, and sulphur (1.4 g.) were heated for 8 hr. at 140° ± 1° *in vacuo* (cf. Bloomfield, *J.*, 1947, 1546). The product was distilled in a short-path still for 8 hr. at 140°, and the infra-red spectrum of the residual polysulphide examined for cyclic sulphide structures.

Ebonite.—Samples containing ~32% of sulphur were prepared from pale crepe by Mr. R. I. Wood, in very thin sheets suitable for spectroscopic examination. No auxiliary accelerators or ebonite dust were incorporated. The infra-red spectra of 5-hr. and 30-hr. vulcanisates were identical and unaltered by acetone extraction. The ebonite spectra were compared with those of the cross-linked sulphide (XIV) from (I) and of squalene polysulphide. Distinct similarities were apparent, in particular a band at 945 cm.^{-1} in (XIV), 953 cm.^{-1} in squalene polysulphide, and 947 cm.^{-1} in ebonite, of quite similar shape and intensity in all three which was not present in the pure hydrocarbons. The band appeared to be related to the $958, 942\text{ cm.}^{-1}$ doublet in (VI) and to the 947 cm.^{-1} band in (IX), strongly suggesting the presence of this type of grouping.

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BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48 TEWIN ROAD, WELWYN GARDEN CITY, HERTS.

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