

578. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part VIII.*¹ *The Reaction of Sulphur with Mono-olefins.*

By L. BATEMAN, R. W. GLAZEBROOK, C. G. MOORE, M. PORTER, G. W. ROSS, and R. W. SAVILLE.

Reaction of sulphur with mono-olefins at 140° gives, not only alkenyl alkyl polysulphides as previously supposed, but also substantial amounts of more saturated compounds having two attachments of sulphur per olefin moiety. The latter appear to have mainly cyclic structures (derived from the linking of two ethylenic centres) and include polymeric polysulphides (derived from similar linking of three or more olefin units); epithio-groups could not be detected in these polysulphides. The proportion of alkenyl alkyl polysulphide to these other products varies in a regular manner among different types of olefin.

The mechanistic significance of these findings is discussed in Part XI.

Introduction to Parts VIII—XI.—Earlier Parts of this series¹⁻⁶ reported the partial separation and identification of the complex products of certain sulphur-olefin and related reactions chosen as models for examining the mechanism of vulcanisation of natural and synthetic rubbers by sulphur. The main conclusion was that sulphur-olefin interaction proceeds by free-radical chain processes, and this has been quoted elsewhere⁷ and widely accepted.

Results are now presented which extend and correct the earlier findings and lead to the different mechanistic conclusion that the reactions are *polar* in type, involving heterolysis of S-S and C-H bonds. This paper and Part IX⁸ deal with the products of the reactions of sulphur with mono-olefins and a 1 : 5-diolefin, respectively, and Part X⁹ presents a complementary kinetic investigation, the first for such reactions. All the experimental evidence is collated in Part XI¹⁰ in a general theory of sulphur-olefin interaction.

Reaction of Sulphur with Mono-olefins at about 140°.—Previous workers^{2,11,12} have reported that the products are mainly polysulphides $R \cdot S_x \cdot RH_2$ in which the hydrocarbon attachments are alkenyl (R) and alkyl (RH_2), as deduced from elementary analyses and from the results of degradation with ozone.¹¹ Ozonisation was, however, of limited diagnostic value, since the method was applied before the response of different sulphide units to ozone had been ascertained.¹³ The comparable use of methyl iodide¹⁴ is also inadmissible since its reaction with sulphides to yield trimethylsulphonium iodide is non-specific¹⁵ with respect to the structures of R and R' in $R \cdot S \cdot R'$ and occurs to negligible extent with di- and poly-sulphides.¹⁶

¹ Part VII, Farmer, Ford, and Lyons, *J. Appl. Chem.*, 1954, **4**, 554.

² Farmer and Shipley, *J.*, 1947, 1519.

³ Naylor, *J.*, 1947, 1532.

⁴ Bloomfield, *J.*, 1947, 1546.

⁵ *Idem*, *ibid.*, p. 1547.

⁶ *Idem*, *J. Soc. Chem. Ind.*, 1949, **68**, 66.

⁷ Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, 1953, p. 454; Burnett, "Mechanism of Polymer Reactions," Interscience Publ. Inc., New York, 1954, p. 89; Grassie, "The Chemistry of High Polymer Degradation Processes," Butterworths, London, 1956, p. 246.

⁸ Bateman, Glazebrook, and Moore, following paper.

⁹ Ross, Part X, this issue.

¹⁰ Bateman, Moore, and Porter, Part XI, this issue.

¹¹ Armstrong, Little, and Doak, *Ind. Eng. Chem.*, 1944, **36**, 628.

¹² Selker and Kemp, *ibid.*, 1947, **39**, 895.

¹³ Barnard, *J.*, 1957, 4547.

¹⁴ Selker and Kemp, *Ind. Eng. Chem.*, 1944, **36**, 16.

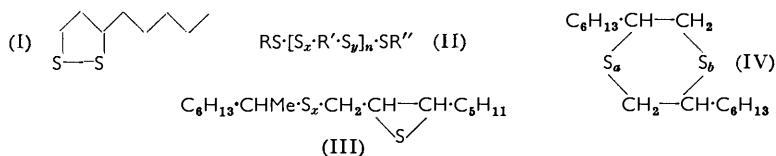
¹⁵ Bloomfield, Proc. 2nd Rubber Tech. Conf., London, 1948, p. 79.

¹⁶ Selker, *Ind. Eng. Chem.*, 1948, **40**, 1467.

The products of the sulphuration of differently substituted alkenes (oct-1-ene, cyclohexene, hept-2-ene, 2-methylpent-2-ene, 1-methylcyclohexene, and 2 : 6-dimethyloct-2-ene) have now been examined in greater detail, and their structures determined by a combination of conventional analyses, hydrogenolysis by reaction with lithium aluminium hydride,¹⁷ and spectroscopic comparison of original and hydrogenolysis products with synthetic reference compounds.

Reaction of Sulphur with Oct-1-ene.—At 140° complete combination of the sulphur (0.350 g.-atom/mole) occurs in 14 hr. (see also Part X).⁹ The product consisted of (i) unchanged olefin, spectroscopically identical with the original material, (ii) a small quantity of a volatile sulphur compound, probably 1 : 2-epithio-octane, and (iii) the main product, "octene polysulphide."

The polysulphide had an average composition (C₈H_{16.1}S_{2.33})_{2.12}, apparently indicative of two octene units joined by a polysulphidic link, with the retention of the H : C ratio of the original olefin. The inference that on average one octyl and one octenyl group are present per molecule (cf. refs. 2 and 12) is, however, incorrect since the infrared spectrum showed the polysulphide to be predominantly saturated, there being no vinylic (CH₂:CHR) unsaturation and a maximum of 0.22 double bond as *trans*-CHR:CHR' group per molecule. On hydrogenolysis, only 45% of the total sulphur was liberated as hydrogen sulphide (an octenyl octyl polysulphide of the above composition should yield *ca.* 60%), and the remainder was located in (a) a monothiol fraction, mainly octane-2-thiol with a minor amount of an unsaturated thiol having *trans*-CHR:CHR' groups, (b) octane-1 : 2-dithiol, (c) a monosulphide comprising dioctyl and/or octenyl octyl sulphide, and (d) a high-boiling fraction whose analyses indicated formula (C₈H_{15.6}S_{1.0})_{2.4}. No evidence for the presence of octane-1 : 3-dithiol could be obtained; oxidation of the dithiol fraction and attempts to detect the formation of the disulphide (I) by the characteristic ultraviolet absorption of the 1 : 2-dithiolan ring system¹⁸ were unsuccessful.



On less complete evidence, it had previously been inferred¹⁹ that the dithiol results from the hydrogenolysis of polymeric polysulphides typified by (II). The observed composition of the bulk polysulphide precludes the presence of appreciable amounts of such structures unless (i) the ebullioscopic method for determining the molecular weight gives an erroneously low value, or (ii) products of low molecular weight, containing only one olefinic unit per molecule, are also present. Both these possibilities have been investigated and must be dismissed: the ebullioscopic method shows no anomalous features when applied to authentic di- and poly-sulphides, and fractionation of the total polysulphide yields no material containing single olefin units. Further, the relative molar yield of mono- and di-thiols of 1 : 1 is incompatible with their derivation from a structure (II). The dithiol could result from hydrogenolysis of an alkenyl alkyl structure C₈H₁₇·S_x·C₈H₁₅ (one double bond), followed by combination of the hydrogen sulphide and octenethiol produced, but this would be at variance with the spectroscopic data, and with negative results from experiments to test the formation of dithiols by secondary reactions during the hydrogenolysis of authentic alkenyl alkyl and dialkenyl polysulphides. Thus, the hydrogenolysis of di(cyclohex-2-enyl) polysulphide gives solely hydrogen sulphide and cyclohex-2-ene-1-thiol.

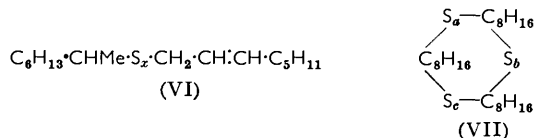
¹⁷ Arnold, Lien, and Alm, *J. Amer. Chem. Soc.*, 1950, **72**, 731; Moore and Saville, *J.*, 1954, 2082.

¹⁸ Barltrop, Hayes, and Calvin, *J. Amer. Chem. Soc.*, 1954, **76**, 4348.

¹⁹ Bateman, Glazebrook, Moore, and Saville, Proc. 3rd Rubber Tech. Conf., London, 1954, p. 298.

The only remaining explanation is that the dithiol is primarily derived from products composed of two hydrocarbon units joined by sulphur bridges in such a way that one or both units have more than one sulphur attachment, *i.e.* (III) or (IV). On hydrogenolysis, a compound (IV) would yield only the observed octane-1 : 2-dithiol, but a compound (III) would be expected to give the 1 : 2- and the 1 : 3-isomers unless scission of the epithio-ring is specifically oriented. Such orientation is unlikely, and positive evidence favouring structure (IV) has been obtained by treating the polysulphide with potassium hydrogen sulphide. A product (V), $(C_8H_{16.1}S_{1.4})_3$, resulted, which was practically free from thiol groups and polysulphide units greater than S_2 . Hydrogenolysis of product (V) yielded a C_8 thiol, octane-1 : 2-dithiol, dioctyl and/or octenyl octyl sulphide, and a polymer $(C_8H_{15.3}S_{1.1})_{3.6}$, *i.e.*, products similar to those obtained likewise from the parent polysulphide. The observed transformations are consistent with the attack of HS^- ions on the S-S bonds in compound (IV), but not with attack on a structure (III), which would give, *inter alia*, a product containing free thiol groups, disulphide or shortened polysulphide linkages, and hydrocarbon units with three sulphur atoms directly attached to them, and on hydrogenolysis would give either an octanetrithiol or a dimercaptodioctyl monosulphide. Evidence based on other related aspects of episulphide reactivity²⁰ is also against the presence of compound (III).

The monosulphide and the high-boiling fraction (*d*) obtained after hydrogenolysis of the parent octene polysulphide (p. 2839) appear to be original constituents of the latter and not derived products. The monosulphide is dioctyl sulphide and/or octenyl octyl sulphide, formation of the former paralleling that of dicyclohexyl sulphide in the corresponding sulphuration of cyclohexene.² The fraction (*d*), $(C_8H_{15.6}S_{1.0})_{2.4}$, on the basis of its predominantly saturated nature, its low thiol content, and its resistance to hydrogenolysis



(confirmed by independent experiment) appears to be mainly compound (IV; $a = b = 1$), mixed with minor amounts of compound (II; $x = y = 0$; $n = 1$) and a mercaptomono-sulphide, $C_8H_{17} \cdot S \cdot C_8H_{16} \cdot SH$, the latter being derived from (II; $x = 0$, $y \geq 1$; $n = 1$). The resistance of the C-S bonds in compounds (IV; $a = b = 1$) and (II; $x = y = 0$; $n = 1$) to hydrogenolysis is comparable with the resistance of C-S bonds in monosulphides and in the polymer $(C_8H_{16}S)_n$ obtained from 1 : 2-epithio-octane.²⁰

After allowance for loss on isolation, the yields of hydrogenolysis products recorded in Table I allow a semi-quantitative analysis of the octene polysulphide to be made as follows: octenyl octyl polysulphide (VI; $x = 6.7$), 25 mole %; (IV; $a + b = 6.7$), 30 mole %; dioctyl- and/or octenyl octyl sulphide, 15 mole %; (II; $R = R' = R'' = C_8$; $x + y = 4.7$, $n = 1$), 15 mole %; and a mixture of (IV; $a = b = 1$) and (II; $R = R' = R'' = C_8$; $x = y = 0$, $n = 1$), 15 mole %. The elementary analysis and bulk unsaturation of this mixture agree with the above values. Similarly, the product (V) obtained on reaction with hydrosulphide (see above) appears to consist of compounds: (II; $R = R' = R'' = C_8$; $x + y = 3.9$; $n = 1$), 15 mole %; (II; $R = R' = R'' = C_8$; $x + y = 1.95$; $n = 2$), 25 mole %; dioctyl and/or octenyl octyl sulphide, 30 mole %; (VII; $a + b + c = 5.9$), 25 mole %; and non-reducible material $(C_8H_{15.3}S_{1.1})_{3.6}$, 5 mole %. This composition fulfils the analytical requirements and is also in accord with the derivation of (V) from the parent polysulphide.

The above structures, while in agreement with the hydrogenolysis and analytical data, are to some extent arbitrary in respect of molecular complexity and length of the polysulphide linkage. The compositions detailed above should be regarded as typifying the

²⁰ Moore and Porter, *J.*, 1958, 2062.

relative contributions of the various generic structures whose presence is experimentally well founded.

TABLE I. *Yields of hydrogenolysis products from octene polysulphide and the sulphurated product (V) (mole per mole of reactant).*

Reactant	H ₂ S	Mono-thiol	Di-thiol	Mono-sulphide	Residue	Recovery (wt. %)
(C ₈ H _{16.1} S _{2.33}) _{2.12}	2.3	0.62	0.60	0.15	0.17 *	90
(V); (C ₈ H _{16.1} S _{1.4}) ₃	0.16	0.71	1.25	0.30	0.05 †	94

* Average composition (C₈H_{15.6}S_{1.0})_{2.4}. † Average composition (C₈H_{15.3}S_{1.1})_{3.6}.

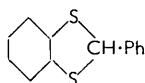
Reaction of Sulphur with sym.-Dialkyl- and Trialkyl-ethylenes.—The average compositions of polysulphides formed from these olefins conform to the pattern observed with oct-1-ene, *viz.*, the major constituents consist of two hydrocarbon units joined by either one or two chains of sulphur atoms, with the C : H ratio of the parent olefin retained (Table 2). Likewise, spectroscopic examination reveals that the total unsaturation present is in all cases less than is required for alkenyl alkyl structures. The residual unsaturation of the several polysulphides is not uniform, however, and varies in the order: 2-methylpent-2-ene > 1-methylcyclohexene > cyclohexene > hept-2-ene > oct-1-ene. (2 : 6-Dimethyloct-2-ene is not included in this series as the spectroscopic analysis is less accurate.)

Hydrogenolysis of the polysulphides gave hydrogen sulphide, mono- and di-thiols containing one olefin unit per molecule, and higher-boiling material containing sulphur-groups resistant to lithium aluminium hydride. The following conclusions can be drawn about the nature of these products: (i) the monothiols are partly unsaturated; (ii) the saturated monothiols derived from the polysulphides of the trialkylethylenes are tertiary; in no case has the secondary isomer been identified; (iii) the dithiols are saturated, and by analogy with the formation of octane-1 : 2-dithiol from "octene polysulphide" are believed to have the thiol groups on vicinal carbon atoms. The dithiol obtained from "cyclohexene polysulphide" gave on treatment with benzaldehyde a phenyldithiolan, m. p.

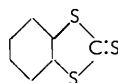
TABLE 2. *Compositions of olefin polysulphides, and yields of hydrogenolysis products (mole per mole of polysulphide).*

Polysulphide from	Formula	Mono-thiol	Dithiol	Molar ratio mono- to di-thiol	H ₂ S	Residue	Recovery (wt. %)
Oct-1-ene	(C ₈ H _{16.1} S _{2.33}) _{2.12}	0.62	0.60	1.1 : 1	2.3	0.32	90
cycloHexene	(C ₆ H _{9.9} S _{2.87}) _{2.1}	0.90	0.53	1.67 : 1	—	0	63
Hept-2-ene	(C ₇ H _{14.0} S _{2.77}) _{2.2}	—	—	—	—	—	—
2 : 6-Dimethyloct-2-ene	(C ₁₀ H _{20.7} S _{2.8}) _{2.18}	1.29	0.90	1.47 : 1	2.88	0	~100
1-Methylcyclohexene ...	(C ₇ H _{12.0} S _{2.68}) _{2.17}	1.14	0.42	2.3 : 1	2.90	0.12	84
2-Methylpent-2-ene	(C ₈ H _{12.0} S _{2.18}) _{2.08}	1.12	0.31	3.7 : 1	2.30	0.05	84

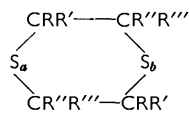
133—134°, different from the hexahydro-2-phenylbenzo-1 : 3-dithiole (VIII), m. p. 115.5° (see Culvenor *et al.*²¹), and yielded a trithiocarbonate, m. p. 99—99.5°, different from the compound (IX), m. p. 169° (see Culvenor *et al.*²²). As the dithiol used by these authors was almost certainly the *trans*-form, it is inferred that the dithiol now obtained is cyclohexane-*cis*-1 : 2-dithiol.



(VIII)



(IX)



(X)

The above findings indicate that the polysulphides listed in Table 2 are composed of constituents similar in type to those present in octene polysulphide, *viz.*, alkenyl alkyl

²¹ Culvenor and Davies, *Austral. J. Sci. Res.*, 1948, 1, A, 236.

²² Culvenor, Davies, and Pausacker, *J.*, 1946, 1050.

polysulphides, cyclic structures (X; R = R' = alkyl; R'' = H or alkyl; R''' = H) analogous to (IV), and polymeric compounds (II). The yields of hydrogen sulphide, mono- and di-thiols, and non-reducible sulphur-compounds obtained on hydrogenolysis (Table 2) show that the polysulphides from the di- and tri-alkylethylenes contain a higher proportion of the alkenyl alkyl polysulphide and a lower proportion of the cyclic and polymeric structures, (X) and (II), respectively, than the products from oct-1-ene. The order in which the alkenyl alkyl polysulphides are formed preferentially is: 2-methylpent-2-ene > 1-methylcyclohexene > cyclohexene > 2 : 6-dimethyloct-2-ene > oct-1-ene, which parallels the order of retention of the olefinic unsaturation in the bulk sulphurated product. As for "octene polysulphide," it is possible to calculate the approximate compositions of those polysulphides for which the product recovery on hydrogenolysis approached 100% (Table 3).

Olefinic Structure of the Polysulphides.—Spectroscopic examination of the "octene polysulphide" shows that the unsaturation present is wholly of the type CHR:CHR', there

TABLE 3. *Approximate compositions of bulk polysulphides (mole fraction).*

Polysulphide from	Alkyl-S _x - alkenyl	(X)	(II)	RSR'	Residual material	Value of x ($a + b$)
2-Methylpent-2-ene	0.80	0.15	0	—	0.05	4.5 ₅
1-Methylcyclohexene	0.60	0.20	0.10	—	0.10	6.1
2 : 6-Dimethyloct-2-ene ...	0.45	0.35	0.20	—	—	6.0
Oct-1-ene	0.25	0.30	0.15	0.15	0.15	6.7

being none of the vinylic type of the parent olefin; only *trans*-CHR:CHR' groups have been identified, but the *cis*-isomer cannot be definitely excluded on the available evidence. This complete double-bond shift is a special feature of the oct-1-ene system which is not observed with the other unsymmetrical olefins studied. The polysulphides from the trialkylethylenes show only minor changes in unsaturation type, there being only small amounts of the CHR:CHR' and CH₂:CRR' forms present. Ultraviolet spectra show the absence of vinyl sulphide groups, C=C·S_x.

EXPERIMENTAL

Preparation of Materials.—Sulphur was purified by Bacon and Fanelli's method.²³ Oct-1-ene and hept-2-ene were Phillips Petroleum Company "Pure Grade" materials. The other olefins were prepared by standard methods and were analytically and spectroscopically pure.

General Procedures—(1) *Hydrogenolysis of polysulphides.* The polysulphide (10 g.) in dry tetrahydrofuran (50 ml.) was added slowly with stirring to lithium aluminium hydride (3—5 g.) in tetrahydrofuran (100 ml.) and the mixture refluxed for 4—6 hr. Excess of reagent was destroyed with ice, and the products were hydrolysed with 2N-sulphuric acid (200 ml.). The thiols were extracted with light petroleum, the extract was washed with water and dried (Na₂SO₄), the solvent was carefully removed through a column, and the thiols were fractionated.

(2) *Determination of "removable sulphur" in polysulphides.* "Removable sulphur," defined as the percentage of total sulphur in the polysulphide liberated as hydrogen sulphide by hydrogenolysis with lithium aluminium hydride, was determined as previously described.¹

(3) *Determination of thiols.* The thiol (10—20 mg.) in aqueous ethanol (100 ml., 95%) was titrated against aqueous 0.01N-silver nitrate and the end-point determined by the amperometric method.²⁴

(4) *2 : 4-Dinitrophenyl sulphide derivatives of thiols.* These were prepared by the method of Bost, Turner, and Norton.²⁵

(5) Molecular weights were determined ebullioscopically in benzene.

²³ Bacon and Fanelli, *Ind. Eng. Chem.*, 1942, **34**, 1043.

²⁴ Kolthoff and Harris, *Ind. Eng. Chem. Analyt.*, 1946, **18**, 161.

²⁵ Bost, Turner, and Norton, *J. Amer. Chem. Soc.*, 1932, **54**, 1985.

(6) *Spectrometric analysis.* Infrared spectra were recorded on a Grubb-Parsons single-beam spectrometer with a rock-salt or lithium fluoride prism, or on a Hilger H.800 spectrometer. Ultraviolet absorption spectra were determined in ethanol or cyclohexane with a Hilger Uvispek spectrophotometer. Unsaturated groups were identified by the characteristic bands of the olefinic $\nu(\text{C}=\text{C})$ and $\delta(\text{CH})$ vibrations,²⁶ and (unless stated otherwise) were estimated in CCl_4 or CS_2 solution by reference to the absorption characteristics of the $\delta(\text{CH})$ band of relevant olefins. Identification of the types of C-S linkages in the polysulphides and their hydrogenolysis products was based on the infrared spectroscopic characteristics of synthetic thiols, sulphides, and polysulphides. The absence of conjugated olefinic unsaturation was based on the absence of absorption at $\sim 2400 \text{ \AA}$; the absence of the $\text{C}=\text{C}\cdot\text{S}_x$ -chromophore in the polysulphides was established by comparison of their ultraviolet absorption characteristics with those of authentic saturated and unsaturated mono- and poly-sulphides.

Reaction of Oct-1-ene with Sulphur.—This is described in detail as illustrative of the procedure used with all the olefins listed on p. 2839. The olefin (101.6 g.) and sulphur (10.16 g.) were heated together *in vacuo* at $140^\circ \pm 0.1^\circ$ for 14.0 hr. No sulphur was deposited from the product during 24 days at -20° . Evaporative distillation of the product at $<50^\circ / <10^{-3} \text{ mm.}$ gave: (i) unchanged olefin (83.09 g.), $n_D^{20} 1.4092$ (Found: C, 85.5; H, 14.3%), which contained only $\text{CH}_2\cdot\text{CHR}$ groups and was devoid of conjugated unsaturation; (ii) a volatile fraction (3.10 g.) which was fractionated further into (iia) oct-1-ene (2.10 g.), $n_D^{20} 1.4095$ (Found: C, 85.8; H, 14.2; S, 0.2%), and (iib) a yellow liquid (0.42 g.) (Found: C, 66.6; H, 10.8; S, 21.9; thiol-S, 0.4. Calc. for $\text{C}_8\text{H}_{16}\text{S}$: C, 66.6; H, 11.2; S, 22.2%), which was predominantly saturated, devoid of thiol and thio-ketone groups, and shown by infrared spectral analysis to be mainly 1:2-epithio-octane; and (iii) "octene polysulphide" (24.84 g.), a dark brown liquid residue, $n_D^{20} 1.5611$ [Found: C, 51.4, 51.7; H, 8.6, 8.8; S, 40.0, 40.3; "Removable sulphur," 44.8, 45.3%; M , 412, 410. Corresponds to $(\text{C}_8\text{H}_{16.1}\text{S}_{2.33})_{2.12}$], which was largely saturated.

The polysulphide (iii) (10.02 g.) with lithium aluminium hydride (4.76 g.) gave the following thiol fractions: (iiia) b. p. $71\text{--}75^\circ / 17 \text{ mm.}$, $n_D^{20} 1.4564$ (2.09 g.) (Found: C, 66.0; H, 12.0; S, 21.9; thiol-S, 22.6; C:H, 8:17.3. Calc. for $\text{C}_8\text{H}_{16}\text{S}$: C, 66.6; H, 11.2; S, 22.2. Calc. for $\text{C}_9\text{H}_{18}\text{S}$: C, 65.7; H, 12.4; S, 21.9%); (iiib) b. p. $75\text{--}110^\circ / 17 \text{ mm.}$, $n_D^{20} 1.4817$ (0.26 g.) (Found: thiol-S, 30.8%); (iiic) b. p. $55\text{--}56^\circ / 0.08 \text{ mm.}$, $n_D^{20} 1.5004$ (2.12 g.) (Found: C, 54.5; H, 10.3; S, 35.9; thiol-S, 36.4, 36.6; C:H, 8:18.0. Calc. for $\text{C}_8\text{H}_{18}\text{S}_2$: C, 53.95; H, 10.15; S, 35.95%); (iiid) b. p. $56\text{--}110^\circ / 0.08 \text{ mm.}$, $n_D^{20} 1.4779$ (1.29 g.) (Found: C, 67.6; H, 12.0; S, 20.6; thiol-S, 12.9, 13.2%; M , 220, 240. Calc. for 43:57 mole % mixture of octanedithiol and dioctyl sulphide; C, 67.4; H, 12.2; S, 20.4; thiol-S, 12.3%; M , 224); and (iiie) a residue, $n_D^{20} 1.5075$ (1.42 g.) [Found: C, 65.3; H, 10.7; S, 22.2; thiol-S, $\sim 6\%$; M , 330, 360. Corresponds to $(\text{C}_8\text{H}_{15.6}\text{S}_{1.02})_{2.33}$].

Examination of the hydrogenolysis fractions. Fraction (iiia) was mainly saturated, although absorption at 967 cm.^{-1} could be due to up to 0.20 double bond as *trans*-CHR'CHR' group per mole. Fraction (iiia) gave a 2:4-dinitrophenyl sulphide which was separated chromatographically into: (a) 2:4-dinitrophenyl 1-methylheptyl sulphide, m. p. and mixed m. p. $44\text{--}45^\circ$ (Found: C, 53.7; H, 6.3; N, 8.9. Calc. for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{N}_2\text{S}$: C, 53.8; H, 6.5; N, 9.0%), having an infrared spectrum identical with that of the synthetic material; and (b) an orange-red oil (Found: C, 52.1; H, 6.15; N, 9.1%) which crystallised after 3 months to give 2:4-dinitrophenyl 1-methylheptyl sulphide, m. p. and mixed m. p. $46\text{--}48^\circ$.

The dithiol fraction (iiic) was saturated, weak absorption at 967 cm.^{-1} being attributed to a skeletal vibration also observed in the spectrum of octane-1:2-dithiol. The dithiol was identified as octane-1:2-dithiol by formation of the bis-2:4-dinitrophenyl sulphide which was separated chromatographically into two forms (from ethanol-acetone) having m. p.s and mixed m. p.s $58\text{--}60^\circ$ (Found: C, 46.9; H, 4.35; N, 10.9, 10.8. Calc. for $\text{C}_{20}\text{H}_{22}\text{O}_8\text{N}_4\text{S}_2$: C, 47.1, H, 4.3; N, 11.0%) and $95\text{--}97.5^\circ$ (Found: C, 47.1; H, 4.5; N, 10.7, 10.9%). Recrystallisation of the two forms from acetone at -78° gave the form of m. p. $39\text{--}40^\circ$, and recrystallisation from ethanol-acetone gave other forms, m. p. $61\text{--}62.5^\circ$ and $70.5\text{--}72^\circ$.

Fractions (iiid) and (iiie) were largely saturated; fraction (iiid) contained a saturated dithiol, but other constituents were not identified (conjugated structures were absent).

Hydrogenolysis of fraction (iiie) (1.05 g.) gave hydrogen sulphide (equiv. to 0.4% of "removable sulphur") and the following fractions: (iiiei) b. p. $< 99^\circ / 10^{-2} \text{ mm.}$ (0.08 g.) (Found: C, 62.0; H, 10.8; S, 25.5%); (iiieii) b. p. $99\text{--}100^\circ / 10^{-2} \text{ mm.}$ (0.306 g.) (Found: C, 65.9; H,

²⁶ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, pp. 31 *et seq.*

11.3; S, 22.15%; *M*, 249, 277. Calc. for $C_{16}H_{34}S_2$: C, 66.1; H, 11.8; S, 22.1%; *M*, 291. Calc. for $C_{16}H_{32}S_2$: C, 66.6; H, 11.2; S, 22.2%; *M*, 289, which showed no infrared absorption in the 6μ region but slight absorption at 970 cm^{-1} which could be due to 0.13 *trans*-CHR:CHR' group per mole, whilst the presence of 1.1—1.4 thiol groups per mole was also indicated, and (iii) a residue (0.51 g.) (Found: C, 68.4; H, 10.4; S, 19.3%; *M*, 569, 576) which was mainly saturated and devoid of thiol groups.

Absence of octane-1:3-dithiol in the hydrogenolysis fraction (iiic). Fraction (iiic) (0.879 g.) in light petroleum (40 ml.) was oxidised with excess of iodine in aqueous potassium iodide. The final excess of iodine was destroyed, the organic layer separated, washed with water, and dried (Na_2SO_4), and the solvent removed *in vacuo*, to give a *disulphide polymer* (0.700 g.) [Found: C, 57.2; H, 9.8; S, 32.7%; *M*, 710, 737, 745. $(C_8H_{16}S_2)_4$ requires C, 54.2; H, 9.7; S, 36.1%; *M*, 705] which showed no ultraviolet absorption maximum at 3300 \AA . Comparable oxidation of octane-1:2-dithiol (0.886 g.) gave a disulphide polymer (0.740 g.) (Found: C, 56.0; H, 9.4; S, 34.7%; *M*, 947, 1015) showing no maximum absorption at 3300 \AA . Oxidation of propane-1:3-dithiol in light petroleum gave 1:2-dithiolan having maximum absorption at $3270\text{--}3280\text{ \AA}$. Comparable results to the above were obtained by partial aerobic oxidation of *dilute* ethanolic solutions of fraction (iiic) and propane-1:3-dithiol.

Reaction of "Oct-1-ene Polysulphide" with Potassium Hydrogen Sulphide.—The polysulphide (iii) [Found: C, 52.15; H, 8.65; S, 39.6%; *M*, 427, 405. Corresponds to $(C_8H_{15.8}S_{2.28})_{2.25}$] (8.23 g.) was shaken for 48 hr. at room temperature with an ethanolic solution of potassium hydrogen sulphide [prepared by saturating a solution of potassium hydroxide (7.1 g.) in ethanol (78 ml.) with hydrogen sulphide at 0°]. Ethanol was removed under reduced pressure, and the product treated with water (200 ml.) and extracted with light petroleum ($3 \times 75\text{ ml.}$). Acidification of the aqueous portion with dilute hydrochloric acid gave sulphur (1.37 g., corresponding to 42% of "removable sulphur") but no organic material. Removal of the solvent from the light petroleum extract gave a dark brown liquid (V) (6.76 g.), $n_D^{20} 1.523$ [Found: C, 60.9; H, 10.3; S, 29.2; thiol-S, 0.3; "removable sulphur," 3.9%; *M*, 463, 470. Corresponds to $(C_8H_{16.1}S_{1.41})_{2.97}$], which was devoid of thiol groups and predominantly saturated; absorption at 970 cm^{-1} could correspond to a maximum of 0.17 *trans*-CHR:CHR' unit per molecule. The polysulphide (5.04 g.) with lithium aluminium hydride (1.0 g.) gave the following thiol fractions: (1) b. p. $65\text{--}70^\circ/15\text{ mm.}$, $n_D^{20} 1.4508$ (0.995 g.) (Found: C, 66.6, 67.2; H, 12.3, 12.5; S, 20.0, 20.15; thiol-S, 22.3. Calc. for $C_8H_{16}S$: C, 66.6; H, 11.2; S, 22.2; thiol-S, 22.2. Calc. for $C_8H_{18}S$: C, 65.7; H, 12.4; S, 21.9; thiol-S, 21.9%); (2) b. p. $< 50^\circ/0.08\text{ mm.}$ (0.10 g.); (3) b. p. $56\text{--}57^\circ/0.08\text{ mm.}$, $n_D^{20} 1.4953$ (2.025 g.) (Found: C, 54.7; H, 10.2; S, 35.7; thiol-S, 35.4. Calc. for $C_8H_{18}S_2$: C, 53.95; H, 10.15; S, 35.95; thiol-S, 35.95%); (4) b. p. $60\text{--}80^\circ/0.01\text{ mm.}$ (0.07 g.); (5) b. p. $80\text{--}100^\circ/0.01\text{ mm.}$, $n_D^{20} 1.4811$ (1.12 g.) [Found: C, 67.8; H, 11.8; S, 20.4; thiol-S, 9.2%; *M*, 245, 256. Corresponds to $(C_8H_{16.6}S_{0.90})_{1.77}$. Calc. for 38: 62 mole % mixture of octanedithiol and dioctyl sulphide: C, 68.1; H, 12.4; S, 19.5; thiol-S, 10.8%; *M*, 228]; (6) a residue, $n_D^{20} 1.525$ (0.30 g.) [Found: C, 64.2; H, 10.3; S, 23.6%; *M*, 510, 543. Corresponds to $(C_8H_{16.3}S_{1.10})_{3.58}$]. The infrared spectra of fractions (1), (3), (5), and (6) closely resembled those of the corresponding fractions from the hydrogenolysed unchanged polysulphide with the exception that *all* fractions were predominantly saturated.

Evaporative Distillation of "Oct-1-ene Polysulphide."—Distillation of the polysulphide $(C_8H_{15.8}S_{2.28})_{2.25}$ (1.986 g.) at $100^\circ/10^{-2}\text{ mm.}$ in a pot-type "molecular still" ¹² gave (1) an orange liquid (0.231 g.) (Found: C, 66.1; H, 11.2; S, 22.45%; *M*, 269, 257. Calc. for $C_{16}H_{32}S_2$: C, 66.6; H, 11.2; S, 22.2%; *M*, 289. Calc. for $C_{16}H_{34}S_2$: C, 66.1; H, 11.8; S, 22.1%; *M*, 291), and (2) an orange liquid (0.121 g.) (Found: *M*, 376, 343). Distillation was continued at 10^{-5} mm. (bath-temp. up to 115°) to give fractions (3) an orange liquid (0.598 g.) [Found: C, 47.9; H, 8.3; S, 43.7%; *M*, 493, 450. Corresponds to $(C_8H_{16.5}S_{2.74})_{2.4}$], (4) an orange-brown liquid (0.429 g.) [Found: C, 47.45; H, 8.1; S, 44.7%; *M*, 520, 483, 462. Corresponds to $(C_8H_{16.3}S_{2.82})_{2.4}$], and (5) a dark brown residue (0.352 g.) [Found: C, 54.05; H, 9.8; S, 36.6%; *M*, 843, 800. Corresponds to $(C_8H_{17.3}S_{2.03})_{4.6}$]. Recovery of the polysulphide was 87%. All fractions were spectroscopically similar to the parent polysulphide.

Synthesis of Reference Compounds for the Oct-1-ene Reaction.—(1) *Octane-1-thiol* (cf. Brown, Jones, and Pinder ²⁷). 1-Acetylthio-octane, b. p. $116\text{--}117^\circ/10\text{ mm.}$, $n_D^{20} 1.4641$ (64%) (Found: C, 63.7; H, 10.6; S, 16.8. Calc. for $C_{10}H_{20}OS$: C, 63.9; H, 10.65; S, 17.0%), was prepared

²⁷ Brown, Jones, and Pinder, *J.*, 1951, 2123.

by addition of thiolacetic acid to oct-1-ene. Hydrolysis of the thiolester with aqueous-ethanolic potassium hydroxide under nitrogen gave octane-1-thiol, b. p. 77—78°/10 mm., n_D^{20} 1.4542 (85%) (Found: C, 65.65; H, 12.2; S, 21.2. Calc. for $C_8H_{18}S$: C, 65.7; H, 12.4; S, 21.9%). The 2:4-dinitrophenyl octyl sulphide had m. p. 75—76° [from light petroleum (b. p. 60—80°)] (Found: C, 54.2, 54.1; H, 6.5, 6.4; N, 9.15. Calc. for $C_{14}H_{20}O_4N_2S$: C, 53.9; H, 6.4; N, 9.0%) (Brown *et al.* report m. p. 78°). The mercuric salt crystallised as plates (from ethanol), m. p. 71—72° (Found: C, 39.15; H, 6.95. Calc. for $C_{16}H_{34}S_2Hg$: C, 39.1; H, 6.95%).

(2) *Octane-2-thiol*. This thiol, b. p. 64—65°/10 mm., n_D^{20} 1.4506 (79%) (Found: C, 66.1; H, 12.4; S, 20.7%), was prepared from 2-bromo-octane and thiourea by the normal method.²⁸ It gave 2:4-dinitrophenyl 1-methylheptyl sulphide, m. p. 44.5—45° (from ethanol) (Found: C, 53.75; H, 6.3; N, 8.8%) (Norman, LeSuer, and Mastin²⁹ report m. p. 47.5°).

(3) *Octane-1:2-dithiol*. A solution of potassium ethyl xanthate (33.6 g.) in acetone (700 ml.) was filtered from insoluble material and then added with stirring during 1 hr. to 1:2-dibromo-octane (19.0 g.; b. p. 53—56°/0.15 mm.; n_D^{20} 1.4969) in acetone (35 ml.). The product was filtered, the solvent removed, the yellow residue dissolved in chloroform (50 ml.), washed with water, and dried (Na_2SO_4), and the solvent removed under reduced pressure. The resulting xanthic ester in dry tetrahydrofuran (50 ml.) was hydrogenolysed for 4 hr. by lithium aluminium hydride (7.6 g.) in refluxing tetrahydrofuran (75 ml.) (cf. Djerassi *et al.*³⁰), to give *octane-1:2-dithiol* (4.3 g., 35%), b. p. 56—59°/0.05—0.1 mm., n_D^{20} 1.4981 (Found: C, 54.0; H, 10.1; S, 36.1; thiol-S, 35.1. $C_8H_{18}S_2$ requires C, 53.95; H, 10.15; S, 35.95; thiol-S, 35.95%). The dithiol showed a weak infrared band at 967 cm^{-1} . The *bis-2:4-dinitrophenyl sulphide* exhibited polymorphism, being obtained in a number of forms whose colour and m. p. depended on the conditions of crystallisation. Thus, slow crystallisation from dilute ethanol-acetone solution gave a pale yellow solid, m. p. 56—57°, whereas more concentrated solutions gave deep yellow crystals, m. p. within the ranges 97—98°, 92—94°, and 70—72°. Satisfactory analyses were obtained for all forms (*e.g.*, form of m. p. 97—98°: Found: C, 47.0; H, 4.3; N, 10.95. $C_{20}H_{22}O_8N_4S_2$ requires C, 47.1; H, 4.3; N, 11.0%). Crystallisation from concentrated acetone solutions at -78° gave a form, m. p. 38—38.5°, which changed in 1 month into the form, m. p. 71.5—73°. Attempted preparation of other derivatives of the dithiol for diagnostic purposes was unsuccessful; the *bis-(2:4-dinitrophenyl sulphone)* was unstable, and the trithiocarbonate and benzylidene derivative were oils.

Reaction of Sulphur with Di- and Tri-alkylethylenes.—The olefin and sulphur (10% w/w) were heated together *in vacuo* at 140° for 5 hr. The products were isolated and examined as described above for the oct-1-ene-sulphur reaction. The major experimental findings are summarised in Tables 2 and 3 and in the text (pp. 2841—2).

Synthesis of Reference Compounds.—(1) *Di(cyclohex-2-enyl) polysulphide*. Reaction of cyclohex-2-enethiol (7.0 g., b. p. 44—46°/10 mm.) with sulphur (3.0 g.) in the presence of a trace of diethylamine at room temperature gave the polysulphide (8.0 g.) [Found: C, 48.3; H, 5.95; S, 45.8; "removable sulphur," 47.0%; *M*, 300, 316. Corresponds to $(C_6H_{8.9}S_{2.15})_{2.05}$]. Hydrogenolysis of the polysulphide (5.0 g.) yielded only hydrogen sulphide and cyclohex-2-enethiol (2.93 g.), b. p. 48—50°/10 mm., n_D^{20} 1.5242 (Found: C, 63.3; H, 8.8; S, 27.8. Calc. for $C_6H_{10}S$: C, 63.1; H, 8.8; S, 28.1%).

(2) *2:6-Dimethyloctane-2-thiol*. 2-Benzylthio-2:6-dimethyloctane (74%; b. p. 100—112°/0.01 mm., n_D^{20} 1.5147) was prepared by the sulphuric acid-catalysed addition of toluene- ω -thiol to 2:6-dimethyloct-2-ene (cf. ref. 31). Reduction of the sulphide with sodium in liquid ammonia (cf. ref. 31) gave 2:6-dimethyloctane-2-thiol (91%), b. p. 84—85°/10 mm., n_D^{20} 1.4543 (Found: C, 68.9; H, 12.65; S, 18.35. $C_{10}H_{22}S$ requires C, 69.0; H, 12.6; S, 18.4%).

(3) *2:6-Dimethyloctane-3-thiol*. 2:6-Dimethyloct-2-ene (14 g.) reacted exothermically with mercaptoacetic acid (10 ml.) under ultraviolet light to give 3-acetylthio-2:6-dimethyloctane, b. p. 117—118°/10 mm., n_D^{20} 1.4670 (18.5 g., 86%) (Found: C, 66.1; H, 11.05; S, 15.35. Calc. for $C_{12}H_{24}OS$: C, 66.7; H, 11.1; S, 14.8%). Hydrolysis of the thiolester (18.4 g.) with boiling aqueous-ethanolic potassium hydroxide during 30 min. gave 2:6-dimethyloctane-3-thiol, b. p. 88—89°/10 mm., n_D^{20} 1.4584 (13.2 g., 89%) (Found: C, 69.0; H, 12.7; S, 18.4; thiol-S, 18.4%).

²⁸ *Org. Synth.*, 1941, **21**, 36.

²⁹ Norman, LeSuer, and Mastin, *J. Amer. Chem. Soc.*, 1952, **74**, 161.

³⁰ Djerassi, Gorman, Markley, and Oldenburg, *J. Amer. Chem. Soc.*, 1955, **77**, 568.

The synthesis of other reference compounds has been described previously.³¹

Thermal Stability of Olefin Sulphuration Products.—Samples of "olefin polysulphides" were heated *in vacuo* at 140° for 5 hr. Elementary and spectroscopic analysis of the products revealed the changes in molecular constitution and complexity as tabulated.

No.	Polysulphide from	Original composition	No.	Composition after heating
1	Oct-1-ene	(C ₈ H _{15.8} S _{2.28}) _{2.25}	1a	(C ₈ H _{16.1} S _{2.28}) _{2.83}
2	2-Methylpent-2-ene	(C ₈ H _{12.0} S _{2.18}) _{2.06}	2a	(C ₈ H _{12.1} S _{2.21}) _{2.41}
3	1-Methylcyclohexene	(C ₇ H _{12.0} S _{2.68}) _{2.17}	3a	(C ₇ H _{12.1} S _{2.86}) _{2.27}
4	2 : 6-Dimethyloct-2-ene	(C ₁₀ H _{20.7} S _{2.8}) _{2.18}	4a	(C ₁₀ H _{20.6} S _{2.76}) _{1.81}

Polysulphides 1 and 1a had similar spectra except for slightly less pronounced absorption at 970 cm.⁻¹ in the latter. Samples 2 and 2a had similar spectra except for some reduction in trialkylethylenic unsaturation; comparable differences were shown between 3 and 3a, and 4 and 4a.

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THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48-56 TEWIN ROAD,
WELWYN GARDEN CITY, HERTS. [Received, December 23rd, 1957.]

³¹ Moore and Saville, *J.*, 1954, 2089.