

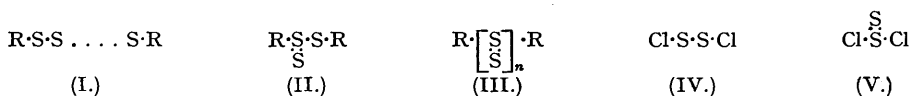
302. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part IV. The Thermal Decomposition of Organic Polysulphides, and its Contribution to the Sulphur-Olefin Reaction.*

By GEORGE F. BLOOMFIELD.

At temperatures in the region of 140° organic polysulphides undergo disproportionation resulting from thermal fission of S-S bonds and recombination of the fission products. In the presence of olefins a considerable proportion of the fission products become attached to ethylenic centres of the olefin, forming mixed mono- and poly-sulphides. The major part of the monosulphide product is fully saturated, hydrogen-capture occurring during, or subsequent to, the formation of adducts from the olefin and sulphurated fragments; unsaturation, however, appears in the polysulphide portion. The polysulphides are capable of producing monothio-cross-links between the original olefinic molecules only in so far as they are able to yield up elementary sulphur to the olefin, and when the original olefin is a polyisoprene the tendency towards the formation of a high proportion of intramolecular cyclic sulphide still further reduces the opportunity for formation of intermolecular sulphur-cross-linked products.

SINCE polysulphides are the principal products of the reaction of sulphur with olefins (Farmer and Shipley, Part I, this vol., p. 1519) an understanding of their thermal stability and of their further reaction with olefins is clearly of importance in clarifying the general problem of chemical changes associated with the olefin-sulphur reaction and the related problem of rubber vulcanisation.

The structure of polysulphides has long presented difficulty in respect of the necessity for deciding between their representation by the wholly linear structures (I) or by co-ordinated structures of type (II) or (III). Based principally on evidence provided by X-ray data (Katz,



Trans. Faraday Soc., 1936, **32**, 77) and by the lability of a considerable proportion of the sulphur atoms on treatment with alkali (Patrick, *ibid.*, p. 347) or with sodium sulphite (Parker, *India Rubber J.*, 1945, **108**, 387), a co-ordinated structure has been generally assigned to those polysulphides obtained by the interaction of organic halides and alkali polysulphides. Evidence based on the lability of sulphur atoms is, however, no certain criterion of the presence of co-ordinated sulphur atoms, since it is now shown that a comparable lability is exhibited by *two* of the four sulphur atoms in tetrasulphides obtained by the interaction of thiols and sulphur monochloride. Whether one accepts a linear (IV) or branched (V) structure for sulphur monochloride, it follows that three of the four sulphur atoms of the derived tetrasulphide must be in a linear chain, so that when two sulphur atoms are removed, at least one of them must have been abstracted from a linear chain. The electron-diffraction investigations of Palmer (*J. Amer. Chem. Soc.*, 1938, **60**, 2360) indicate the linear structure (IV) for the monochloride, and since, moreover, a recent ultra-violet absorption study by Koch (in the press) provides convincing evidence of a linear structure of some of the organic polysulphides which form the basis of the present work, it seems fully justifiable to assume linear structures both for the tetrasulphides prepared by the interaction of thiols with sulphur monochloride and for the polysulphide products of the sulphur-olefin reaction. The chemical behaviour of these poly-

sulphides is not at variance with the assumption of a linear structure, nor is a linear structure inconsistent with the ring formulation of the polymeric organic polysulphides (Fuller, *Chem. Reviews*, 1940, **26**, 160).

The precise mechanism of the removal of sulphur from polysulphides by sodium sulphite or sodium hydroxide is not altogether clear, although when the former reagent is used it appears certain that the polysulphide is converted mainly into disulphide (Armstrong, Little, and Doak, *Ind. Eng. Chem.*, 1944, **36**, 628) although a small proportion (not exceeding 10%) of it undergoes reduction to thiols. Probably there is fission of the sulphur chain, giving thio-radicals which recombine to form disulphides, or, to a small extent, are reduced to thiols, while the sulphur liberated converts sodium sulphite into thiosulphate.

Although the thermal decomposition at 170—180° of some polysulphides containing olefinic unsaturation gives thiols and hydrogen sulphide, together with a sulphurated product of much reduced hydrogen content (Farmer and Shipley, Part I), it is now found that the thermal decomposition of a saturated tetrasulphide at somewhat lower temperatures (140—150°) gives only disproportionation products (lower and higher polysulphides), neither thiol nor hydrogen sulphide being formed. Moreover, at temperatures below 120°, the tetrasulphides could generally be distilled unchanged.

Interaction of a polysulphide $R \cdot S_x \cdot R$ with *cyclohexene* in the temperature range 140—180° gave sulphurated products of the type $R \cdot S_y \cdot R'$ ($y < x$) in which R was an organic group from the original polysulphide and R' was *cyclohexyl* or *cyclohexenyl*, together with disulphides R_2S_2 derived from the original polysulphide, and *cyclohexyl cyclohexenyl* di- and poly-sulphides. The latter were similar to the polysulphides resulting from the reaction of sulphur itself with *cyclohexene*, but contained a smaller sulphur chain. Diethyl tetrasulphide and *cyclohexene* yielded rather complex mixtures in which the more volatile components could not be adequately separated by distillation, so it was not possible to confirm or to exclude the presence of either the *cyclohexanethiol* or the *cyclohexene episulphide* expected from the work of Jones and Reid (*J. Amer. Chem. Soc.*, 1938, **60**, 2452). The presence of some *cyclohexyl ethyl sulphide* was, however, established beyond doubt by the isolation of *cyclohexyl ethyl sulphone* on oxidation of the most volatile portion of the reaction product. When polysulphides containing larger organic groups were used, the separation of volatile components was facilitated, although the separation of non-volatile components became correspondingly more difficult. In spite of the most careful search, *cyclohexene episulphide* could in no case be detected, and the total amount of *cyclohexanethiol* formed, together with thiols derived from the original polysulphide, was extremely small. The most volatile products in every instance consisted of mixed mono-sulphides of the type $C_6H_{11}S \cdot R$, R being an organic group of the original tetrasulphide, although when *di-p-chlorophenyl tetrasulphide* reacted with *cyclohexene* some *dicyclohexyl sulphide* was formed in addition to *p-chlorophenyl cyclohexyl sulphide*. The origin of the *dicyclohexyl sulphide* in the latter case is obscure.

Unsaturated polysulphides obtained by reaction of sulphur with *cyclohexene* reacted at 140° with further *cyclohexene* to give polysulphides with shorter sulphur chains, separable into components none of which appeared to be of greater sulphur chain-length than a tetrasulphide, with an increasing tendency towards saturation in the more volatile components. The amount of material available did not, however, permit of the isolation of a monosulphide.

It is accordingly suggested that the thermal decomposition of polysulphides at temperatures below 180° involves thermal fission of $-S-S-$ bonds. In the absence of a second reactive substance, recombination of fission products regenerates the polysulphides or gives disproportionation products by union of dissimilar fission products. In the presence of an olefin the fission products (or the thiols derived therefrom by hydrogen capture) may either add to the ethylenic linkage, forming, ultimately, a saturated sulphide, or the fission product may link with an allylic radical to form an unsaturated mono-, di-, or poly-sulphide. Simultaneously, reaction occurs between the olefin and sulphur liberated from the sulphur chain of the polysulphide, and since the sulphur may be presumed to be liberated in a rather reactive (possibly atomic) form, the length of the sulphur chain in these products is not large.

It follows that in the reaction of sulphur with olefins, secondary products resulting from the reaction of primarily-formed polysulphides with the olefins are to be expected, especially when the olefin is present in considerable excess. When polysulphides reacted with dihydromyrcene, a considerable quantity of dihydromyrcene cyclic sulphide, identical with that obtained from dihydromyrcene and sulphur (Farmer and Shipley, Part I), was formed. Of particular interest from the point of view of the general reaction of sulphur with polyisoprenes is the ready formation of the cyclic sulphide when dihydromyrcene polysulphide itself was heated with dihydro-

myrcene, and it is hoped soon to ascertain whether the cyclic sulphide formed in the reaction of polyisoprenes with sulphur is a primary product of the olefin-sulphur reaction, or a secondary product formed solely by interaction of polyisoprene polysulphides with the excess of hydrocarbon usually present in these reactions.

Since it is now generally accepted that rubber vulcanisation requires the presence of intermolecular cross-linkages, the combination with rubber of sulphurated fragments of polysulphides alone should not cause vulcanisation unless the sulphurated fragments are themselves polyfunctional (cf. Patrick, U.S.P. 2,235,621). Dialkyl tetrasulphides react fairly readily with rubber, giving *soluble* products containing 2 or 3 units % of combined sulphur which is undoubtedly contained in sulphurated polysulphide fragments added at ethylenic centres of the rubber, since it is well established that products of the reaction of sulphur with rubber, containing considerably less combined sulphur, are quite insoluble. Both the H:C ratio and loss of unsaturation in these tetrasulphide-rubber reaction products are consistent with the postulated incorporation of sulphurated fission products with the rubber; moreover, the product of interaction of di-*p*-chlorophenyl tetrasulphide with rubber contains chemically-combined chlorine as well as sulphur. The insolubility of the latter product is attributed to the presence of sulphur in excess of that resulting from simple addition of sulphurated polysulphide fragments, and it appears certain that some degree of cross-linking has been brought about by the reaction of sulphur itself, liberated from the sulphur chain of the polysulphide. These ideas are consistent with Throdahl and Beavers's observation (*Rubber Chem. Tech.*, 1945, **18**, 110) that, although dialkyl tetrasulphides are incapable of vulcanising rubber, yet some degree of vulcanisation is observed with certain aromatic polysulphides.

It is known that in dehydrogenation reactions at elevated temperatures disulphides are as effective as sulphur itself, the disulphide linkage undergoing cleavage (Ritter and Sharpe, *J. Amer. Chem. Soc.*, 1937, **59**, 2351). If thermal dissociation of disulphides into RS· radicals (cf. Schönberg, *Ber.*, 1933, **66**, 1932) is appreciable at 140°, then it might be expected that disulphides in the presence of sulphur and an olefin would react essentially as polysulphides, and, furthermore, disulphides themselves might be expected to enter into reaction with olefins. Only scanty evidence of the latter type of reactivity has been obtained with disulphides at temperatures below 180°, and diphenyl disulphide, which might be expected to dissociate rather more readily than dialkyl disulphides, proved to be entirely without action on cyclohexene at 180°. Farmer and Shipley have, however, observed the formation of considerable amounts of mercaptobenzthiazole on heating together benzthiazole disulphide and cyclohexene at 140°. Diethyl disulphide and sulphur, heated together at 140–150°, gave no more than trace amounts of polysulphide, and when there was also an olefinic substance present reaction occurred exclusively between the sulphur and the olefin, giving the usual polysulphide products, without any indication of participation of the dialkyl disulphide.

EXPERIMENTAL.

Microanalyses were carried out by Dr. W. T. Chambers, Miss E. Farquhar, and Miss H. Rhodes. Olefinic unsaturation was determined by bromine addition (Bloomfield, *J. Soc. Chem. Ind.*, 1945, **64**, 274).

All the experiments with polysulphides were conducted in sealed glass tubes or glass flasks.

Preparation of Tetrasulphides.—Tetrasulphides were prepared by a modification of the method described by Bezzi (*Gazzetta*, 1935, **65**, 693). A 10% solution of sulphur monochloride (1 mol.) in carbon disulphide was added at room temperature to a 10% solution of the appropriate thiol (2.1 mols.) in the same solvent, and as soon as the initial brisk evolution of hydrogen chloride had subsided the solution was gently boiled for 30 minutes under a reflux condenser. The solvent was then removed at room temperature under reduced pressure, and, with the exception of di-*p*-chlorophenyltetrasulphide, which crystallised from the residue, the residual tetrasulphide was finally distilled.

Properties of Tetrasulphides.—Diethyl (sample A) had b. p. 58–60°/0.1 mm., n_D^{20} 1.6172; di-*n*-butyl was molecularly distilled at 56° in a falling-film molecular still (Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, **65**, 164) and had n_D^{20} 1.5772; diisooamyl, molecularly distilled at 56°, had n_D^{20} 1.5542; dicyclohexyl, molecularly distilled at 100°, had n_D^{20} 1.6050 (Found: C, 49.0; H, 7.45; S, 43.3. $C_{12}H_{22}S_4$ requires C, 48.95; H, 7.55; S, 43.5%); diphenyl, molecularly distilled at 110°, had n_D^{20} > 1.7; di-*p*-chlorophenyl, recrystallised from light petroleum, had m. p. 57° (Found: C, 40.65; H, 2.35; Cl, 20.3; S, 36.25. $C_{12}H_8Cl_2S_4$ requires C, 41.05; H, 2.30; Cl, 20.2; S, 36.5). The author is also indebted to Dr. F. W. Shipley for a sample (B) of diethyl tetrasulphide, b. p. 45°/0.01 mm., n_D^{20} 1.610, prepared by interaction of ethyl iodide and sodium tetrasulphide. The proportion of the total sulphur content (hereinafter designated "removable sulphur") removable by a boiling 10% aqueous solution of sodium sulphite was determined for each of these tetrasulphides (Table I).

Thermal Decomposition of Dicyclohexyl Tetrasulphide.—The tetrasulphide (17.1 g.) in purified cyclohexane (50 c.c.) was heated for 4 hrs. at 140°, air being excluded. Molecular distillation of the solvent-free product yielded a relatively small amount (2.9 g.) of material of reduced sulphur content which had n_D^{20} 1.5816 (Found: C, 53.7; H 8.35; S, 38.0; removable S, 3 hrs., 25.2, 8 hrs., 31.8%), a considerable amount (9.6 g.) of mainly unchanged dicyclohexyl tetrasulphide, n_D^{20} 1.6032 (Found: C, 49.75;

TABLE I.

Tetrasulphide.	Removable sulphur, % :	
	3 hrs. at 100°.	8 hrs. at 100°.
Diethyl (A).....	50	50
Diethyl (B).....	49	not determined
Di- <i>n</i> -butyl.....	30	45
Diisoamyl.....	44	50
Dicyclohexyl.....	11	44
Diphenyl.....	50	52
Di- <i>p</i> -chlorophenyl.....	50	50

H, 7.55; S, 42.3; removable S, 3 hrs., 9.2; 8 hrs., 37.2%, and a relatively small amount (1.7 g.) of viscous *dicyclohexyl hexasulphide*, n_D^{20} 1.664 (Found: C, 39.8; H, 6.15; S, 53.7; removable S, 3 hrs., 43.2, 8 hrs., 49.2. $C_{12}H_{22}S_6$ requires C, 40.2; H, 6.2; S, 53.6%). The infra-red spectrum of the hexasulphide revealed no unsaturation.

Reaction of Tetrasulphides with Olefins.—(1) *Diethyl tetrasulphide and cyclohexene.* The tetrasulphide (sample A, 20 g.) and cyclohexene (50 c.c.) were heated together for 4 hrs. at 140° in the absence of air. After removal of unchanged cyclohexene (34 g.), the product was separated into a wide range of fractions, b. p. 35–75°/0.1 mm. (total weight 18 g.), leaving a viscous residue (6 g.), care being taken to avoid heating above 130° during the distillation. The recovered cyclohexene contained a trace of ethanethiol, but no carbon disulphide could be detected. Redistillation of the volatile portion of the reaction product gave the following main fractions: (i) b. p. 75–77°/13 mm. (3.5 g.), n_D^{17} 1.5304 (Found: C, 46.05; H, 8.55; S, 46.0; removable S, 2 hrs., 25.9%); (ii) b. p. 77–79°/13 mm. (2.4 g.), n_D^{17} 1.5388 (Found: C, 42.35; H, 8.05; S, 48.95; removable S, 2 hrs., 28.8%); (iii) b. p. 79°/13 mm. (1.4 g.), n_D^{17} 1.5490 (Found: C, 38.4; H, 8.25; S, 53.4; removable S, 2 hrs., 30.5%), and (iv) b. p. 55–75°/0.1 mm. (8.4 g.), n_D^{17} 1.5970 (Found: C, 34.7; H, 6.4; S, 59.3; removable S, 2 hrs., 47.3%). Further fractionation of fraction (iv) gave sub-fractions of unchanged *n*. Since the H : C ratio of fractions (i), (ii), and (iv) indicated the presence of a considerable proportion of cyclohexyl groups, the most volatile fraction (i) was reduced by sodium in alcohol, whereby di- and poly-sulphides were converted into sodium mercaptides. Oxidation with acid permanganate of the alkali-insoluble components of the reduced product gave cyclohexyl ethyl sulphone, m. p. 34° (Found: C, 54.55; H, 9.30; S, 18.1. $C_8H_{16}O_2S$ requires C, 54.55; H, 9.15; S, 18.2%). The non-volatile portion of the original reaction product contained mainly cyclohexyl and cyclohexenyl groups (Found: C, 38.6; H, 5.7; S, 54.5; removable S, 4 hrs., 51%). Only a trace of cyclohexanethiol was detected in the reaction product, and no cyclohexene episulphide was isolated.

(2) *Diisoamyl tetrasulphide and cyclohexene.* The tetrasulphide (17 g.) and cyclohexene (50 c.c.) were heated together for 4 hrs. at 180° in the absence of air. Distillation of the reaction product yielded (a) unchanged cyclohexene (25 c.c.), (b) a fraction, b. p. 60–75°/0.01 mm. (21.2 g.), and (c) a residue (15.7 g.) not distillable below 100°/0.01 mm. The unchanged cyclohexene was carefully redistilled (Fenske column) and the residue was united with traces of liquid of b. p. <60°/0.01 mm. isolated during the preliminary separation; the combined liquids (0.5 g.), redistilled at 13 mm., consisted entirely of thiols (Found: C, 64.8; H, 10.4; S, 24.8; active H, 0.75% = 24.0% S as -SH). Fraction (b) was redistilled at 0.1 mm., and yielded mainly cyclohexyl isoamyl sulphide (12.5 g.), b. p. 58–60°, n_D^{20} 1.4860 (Found: C, 70.2; H, 11.6; S, 18.2; removable S, nil. Calc. for $C_{11}H_{22}S$: C, 71.0; H, 12.0; S, 17.2%), together with the following fractions of higher sulphur content: (i) b. p. 60–62° (2.7 g.), n_D^{20} 1.4909 (Found: C, 69.75; H, 11.45; S, 18.75%); (ii) b. p. 62–65° (0.6 g.), n_D^{20} 1.5018; (iii) b. p. 65–70° (2 g.), n_D^{20} 1.5142 (Found: C, 68.55; H, 10.7; S, 20.5%), and (iv) b. p. 70–75° (2.2 g.), n_D^{20} 1.5218 (Found: C, 65.25; H, 10.2; S, 24.4; removable S, 3 hrs., 12%; *M*, 198; *I. V.*, 46). Permanganate oxidation of the bulk fraction of cyclohexyl isoamyl sulphide gave the sulphone (yield, 60%), m. p. 57–58° (Found: C, 60.25; H, 10.2; S, 14.7%. Calc. for $C_{11}H_{22}SO_2$: C, 60.5; H, 10.2; S, 14.65%), which had mixed m. p. 57° with an authentic specimen of m. p. 57° (Cunneen, this vol., p. 36). The non-distillable residue (c) was passed through the molecular still at 56°, at which temperature about half of the material was volatile. The distillate (6.3 g.), a pale yellow mobile oil, had n_D^{20} 1.5458, and consisted mainly of disulphides (Found: C, 63.8; H, 9.55; S, 26.85; removable S, 8 hrs., 1.5%; *M*, 215). The brown, rather viscous residue (6.1 g.), n_D^{20} 1.5818, was of greater molecular complexity (Found: C, 61.35; H, 8.4; S, 30.0; removable S, 8 hrs., 10.7%; *M*, 318). Infra-red examination of both distillate and residue showed the presence of isoamyl groups, and also revealed the presence of unsaturation of an apparently conjugated type.

A similar experiment conducted at 140° with 12.7 g. of the tetrasulphide gave no cyclohexene episulphide and no more than a trace of thiols. Some cyclohexyl isoamyl sulphide (2.9 g.) was isolated from the crude reaction product; on passing the remainder through the molecular still the volatile portion (7.4 g.), containing considerable unchanged diisoamyl tetrasulphide, had n_D^{20} 1.5481 (Found: C, 48.05; H, 8.55; S, 43.1; removable S, 3 hrs., 37.0; 8 hrs., 43.5%; *M*, 250), but the non-volatile residue (2.1 g.) had n_D^{20} 1.5958 and probably consisted mainly of cyclohexyl isoamyl polysulphide and cyclohexenyl isoamyl polysulphide (Found: C, 43.35; H, 7.0; S, 48.3; removable S, 3 hrs., 45.2; 8 hrs., 53.0%; *M*, 312. Calc. for $C_8H_{11}S_{4.6}C_6H_{10.2}$: *M*, 301). The high proportion of removable sulphur after 3 hrs. at 100° indicates the absence of any appreciable amount of dicyclohexyl tetrasulphide. Treatment of the non-volatile residue with further cyclohexene for 3 hrs. at 140° gave an increase in weight of 23%, and pot-still molecular distillation of the product gave two fractions of substantially lower sulphur content than the original material; the distillate had n_D^{20} 1.5358 (Found: C, 56.7; H, 9.3; S, 33.85; removable S, 3 hrs., 28.7; 8 hrs., 30.7%, corresponding to $C_8H_{11}S_{2.5}C_6H_{10.5}$) and the residue had n_D^{20} 1.6062 (Found: C, 48.95; H, 7.4; S, 42.8; removable S, 3 hrs., 29.7; 8 hrs., 39.2%, corresponding to $C_8H_{11}S_{3.2}C_6H_{10}$).

(3) *Dicyclohexyl tetrasulphide and cyclohexene.* 9.2 G. of the tetrasulphide, heated for 3 hrs. at

180° with excess of *cyclohexene*, gave 9 g. of *dicyclohexyl sulphide* free from unsaturation (Found : C, 72.7; H, 11.2; S, 16.2. Calc. for $C_{12}H_{22}S$: C, 72.7; H, 11.15; S, 16.15%), together with higher sulphides containing unsaturation, *e.g.*, a disulphide (5.8 g.), b. p. >100°/0.01 mm., n_D^{20} 1.5792 (Found : C, 61.6; H, 8.75; S, 29.3%). Oxidation of the *dicyclohexyl sulphide* gave *dicyclohexyl sulphone*, m. p. 132.5°, in 80% yield (Found : C, 62.4; H, 9.7; S, 13.65. Calc. for $C_{12}H_{22}O_2S$: C, 62.55; H, 9.65; S, 13.9%).

(4) *Di-p-chlorophenyl tetrasulphide and cyclohexene*. The product obtained by heating together the tetrasulphide (23.6 g.) and *cyclohexene* (50 c.c.) was separated by one passage through the molecular still at 56° into a pale yellow distillate (A, 14.8 g.) and a golden brown residue (B, 25 g.) which on a second passage through the still at 80° was further separated into a pale yellow distillate (C, 16.0 g.) and a residue (D, 7.3 g.). The distillate A, which had n_D^{20} 1.5661 (Found : C, 65.9; H, 7.8; Cl, 11.25; S, 15.05%), was redistilled from a flask at 0.001 mm., giving the following fractions: (i) b. p. 72–80° (0.8 g.), n_D^{20} 1.5252; (ii) b. p. 80–85° (2.0 g.), n_D^{20} 1.5342 (Found : C, 70.75; H, 9.95; Cl, 3.9; S, 15.3. Calc. for 24.6% $C_{12}H_{15}ClS + 73.4\% C_{12}H_{22}S$: C, 69.0; H, 9.80; Cl, 3.9; S, 15.3%), (iii) b. p. 85–92° (2.7 g.), n_D^{20} 1.5541 (Found : C, 68.45; H, 8.7; Cl, 7.9; S, 15.05. Calc. for 50.5% $C_{12}H_{15}ClS + 49.5\% C_{12}H_{22}S$: C, 68.05; H, 8.9; Cl, 7.9; S, 15.1%), (iv) b. p. 92–96° (4.1 g.), n_D^{20} 1.5762 (Found : C, 65.3; H, 7.05; Cl, 13.95; S, 14.4. Calc. for 89.2% $C_{12}H_{15}ClS + 10.8\% C_{12}H_{22}S$: C, 64.5; H, 7.1; Cl, 13.95; S, 14.3%), and a liquid residue (v), not distillable without overheating, n_D^{20} 1.5808, from which crystallised *p-chlorophenyl cyclohexyl sulphide*, m. p. 25° (Found : C, 63.85; H, 6.8; Cl, 15.75; S, 14.05. $C_{12}H_{15}O_2ClS$ requires C, 63.55; H, 6.7; Cl, 15.65; S, 14.1%). Oxidation of fraction (iv) gave a 62% yield of *p-chlorophenyl cyclohexyl sulphone*, m. p. 68–69° (Found : C, 55.9; H, 5.85; Cl, 13.95; S, 12.4. $C_{12}H_{15}O_2ClS$ requires C, 55.7; H, 5.85; Cl, 13.7; S, 12.4%).

(5) *cyclohexyl cyclohexenyl polysulphide and cyclohexene*. A typical polysulphide (Found : C, 34.55; H, 4.85; S, 59.6%), obtained by the action of sulphur on *cyclohexene*, was heated with an excess of *cyclohexene* for 3 hrs. at 140°. There was a weight increase of 14% and the product yielded a distillate (pot still) which had n_D^{20} 1.5805 (Found : C, 56.1; H, 8.1; S, 36.15; removable S, 8 hrs., 33.2%) and a residue which had n_D^{20} 1.6260 (Found : C, 51.0; H, 7.0; S, 40.9; removable S, 8 hrs., 29.6%).

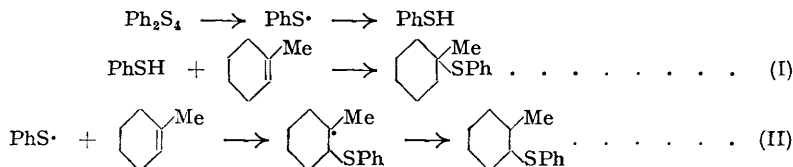
(6) *Diphenyl tetrasulphide and dihydromyrcene*. The tetrasulphide (19.1 g.) and dihydromyrcene (50 c.c.), heated together for 3 hrs. at 150° in the absence of air, yielded dihydromyrcene cyclic sulphide (3.8 g.) and a reddish-brown oil (29.7 g.) which was separated by passage through the molecular still at 80° into a volatile red liquid (21.7 g.) (Found : C, 72.4; H, 7.9; S, 18.7%) which deposited considerable diphenyl disulphide, and a brown viscous residue (4.0 g.) (Found : C, 61.85; H, 7.45; S, 31.7%).

(7) *Dihydromyrcene polysulphide and dihydromyrcene*. The polysulphide (5.5 g.), obtained by the action of sulphur on dihydromyrcene, and freed from cyclic sulphide and free sulphur by repeated passage through the molecular still, was heated with dihydromyrcene (20 c.c.) for 3 hrs. at 145° and yielded 3.3 g. of dihydromyrcene cyclic sulphide together with 6.5 g. of non-volatile matter (Found : C, 57.35; H, 8.6; S, 33.35%).

(8) *Tetrasulphides and rubber*. The tetrasulphides were incorporated into the rubber by milling, the mixtures were heated in sealed evacuated tubes for 3 hrs. at 140°, and the products were extracted with acetone and with chloroform if they were sufficiently insoluble. Diethyl tetrasulphide (0.76 g.) and rubber (5 g.) yielded a reddish-brown product (Found : C, 84.8; H, 11.65; S, 2.8%; I.V., 328) which was soluble in benzene and in chloroform. Di-*p*-chlorophenyl tetrasulphide (1.1 g.) and rubber (4 g.) yielded an insoluble product (Found : C, 79.1; H, 10.45; Cl, 2.65; S, 7.25%).

This paper forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The author expresses his thanks to Dr. E. H. Farmer for his advice and criticism, and to Mr. N. Sheppard for infra-red examination of some of the polysulphides.

Note added in Proof.—Since the above papers were submitted the reaction mechanism involved in the formation of saturated monosulphides by the interaction of polysulphides with olefins has been clarified by a study of the reaction of diphenyl tetrasulphide with 1-methylcyclohexene. Since the major reaction product is phenyl 1-methylcyclohexyl sulphide and not phenyl 2-methylcyclohexyl sulphide it appears certain that the reaction involves hydrogen-capture by the fission product of the polysulphide and addition of the resulting thiol to the double bond by a polar mechanism (I) rather than by a radical addition of the fission product to the double bond followed by hydrogen-capture at the other ethylenic carbon atom (II).



The structure of the sulphide formed was confirmed by mixed m. p. (76°) of the corresponding sulphone with the phenyl 1-methylcyclohexyl sulphone of m. p. 76° described by Cunneen (*loc. cit.*).