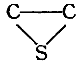
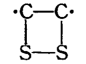
298. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part I. The Reaction of Sulphur with Mono-olefins and with $\Delta^{1:5}$-Diolefins.*

By E. HAROLD FARMER and F. W. SHIPLEY.

The nature of the reaction occurring at 140° between sulphur and two classes of olefins has been investigated. Olefins in general give olefin sulphides, $R{\cdot}S_x{\cdot}R'$, in which on the average half the original unsaturation is lost and x has values up to 6. In the sulphides from mono-olefins R and R′ appear *on average* to be mono-olefinic and saturated respectively, except that some redistribution appears to occur in the sulphides from hydroaromatic mono-olefins owing to the facility of occurrence of (probably secondary) dehydrogenation reactions. $\Delta^{1:5}$-Olefins give in addition to diolefin sulphides, $R{\cdot}S_x{\cdot}R'$, cyclic monosulphides which are formed from only one molecule of olefin. Thus, polyolefins displaying suitably-spaced unsaturation become both inter- and intra-molecularly cross-linked by the sulphur taken into combination. The reaction mechanism is discussed, and it is noteworthy that although substitutive and additive reactions of a radical type play an important role, additive reactions of a polar nature also participate.

THE idea has long been current that sulphur reacts with olefins in an essentially additive manner, although there is no body of evidence in the literature to relate the behaviour of sulphur as a reagent for double bonds with that of any of the numerous common additive reagents. The character of sulphur–olefin reactivity has long been a matter of interest in connexion with the mechanism of vulcanisation of rubbers and of drying oils, but the experiments and speculations of Erdmann (*Annalen*, 1908, **362**, 133), Kirchov (*Kolloid-Z.*, 1913, **13**, 49; 1914, **14**, 35), Prins (*Chem. Weekblad*, 1917, **14**, 932), and many others on this subject have done little to solve the basic problem, as it applies either to high-molecular natural and artificial rubbers or to quite simple olefins such as *iso*butylene and *cyclo*hexene. Episulphides (thioepoxides) and cyclic disulphides containing respectively the groupings (*a*) and (*b*) appear definitely never to have been obtained by the action of sulphur on olefins, and there seems to be no sound evidence to support the view that alternative structures such as (*c*) and (*d*) are formed additively at ethylenic centres.


(*a*.)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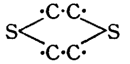
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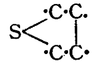
(*d*.)

It is necessary, therefore, to find a new basis for formulating the course of reaction of sulphur, and in this connexion attention turns to the behaviour of the closely related element oxygen, which, also, until recently was regarded as functioning normally as a common additive reagent. Sulphur, like oxygen, contains two unpaired electrons in its outer shell, and since it shows no obvious signs in its recorded behaviour of functioning as a polar reagent it may be suspected of resembling oxygen in possessing an inherent tendency to react apolarly. Hence methods which have been successfully used in the investigation of oxygen-reactivity have been applied to the determination of the principles governing sulphur reactions. In conducting the work it has been necessary, as in the comparable oxygen studies, to divide olefins into four classes, *viz.*, (1) mono-olefins, (2) di- and poly-olefins displaying uni-spaced (*i.e.*, 1 : 4-, 1 : 4 : 7-, etc.) unsaturation, (3) di- and poly-olefins displaying bi-spaced (*i.e.*, 1 : 5-, 1 : 5 : 9-, etc., unsaturation) and (4) conjugated di- and poly-olefins, since the detailed course of reaction is greatly influenced by the unsaturation pattern.

The reaction of sulphur with olefinic materials usually becomes appreciable above 100°, and proceeds at a moderate speed at 140°, which is the most usual vulcanisation temperature for rubbers. This, the lowest temperature at which a convenient speed of reaction is obtained, was adopted for our experiments, not merely because of its common use in industrial vulcanisation processes, but also because experience soon showed that operation at substantially higher temperature is attended by serious danger of confusion arising between primary and secondary reactions. A beginning has been made by the investigation of the reaction between sulphur and *cyclo*hexene, this being of special interest, both because this reaction has twice already been examined by previous workers (Jones and Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2452; Meyer and Hohenemser, *Helv. Chim. Acta*, 1935, **18**, 1061) with results which are difficult to interpret, and because it brings into consideration whatever relationship there may be between the general or ordinary reactivity of sulphur and the possibly specialised reactivity underlying the Vesterberg procedure for the dehydrogenation of hydroaromatic compounds.

Reaction with cyclo*Hexene.*—When *cyclo*hexene is heated with sulphur for several hours in a glass tube or steel autoclave containing air, there is obtained a mixed product composed of sulphurated and unsulphurated materials. The recovered hydrocarbon is wholly unimolecular and contains only a trivial amount of *cyclo*hexadiene and benzene ($<1\%$, determined spectroscopically as benzene), so that simple dehydrogenation of the *cyclo*hexene to a more highly unsaturated state is not an important reaction at 140° (the Vesterberg reaction is usually carried out at 200° and above), unless the *cyclo*hexadiene which is produced is subsequently used up in reaction with sulphur or hydrogen sulphide. The sulphurated products have a very large range of boiling point, but are very sensitive to elevated temperatures, even to those but little higher than the original reaction temperature, so that separation of the products by distillation must be conducted by "molecular" distillation, otherwise progressive (and hitherto unsuspected) thermal degradation sets in, with formation of moderate yields of alkylthiol, dialkyl sulphide, and hydrogen sulphide. If the distillation temperature is kept below 150°, only the merest traces of hydrogen sulphide and thiol are formed, and the main bulk of material is easily separable with tolerable sharpness into a series of polysulphides $R{\cdot}S{\cdot}R'$, $R{\cdot}S_2{\cdot}R'$, $R{\cdot}S_3{\cdot}R'$, and $R{\cdot}S_4{\cdot}R'$. These are the invariable products of reaction under the stated conditions, but they can be progressively broken down at will by being heated for long periods at higher temperatures, and there is no doubt at all that the thiol, hydrogen sulphide, and possibly much of the monosulphide reported by the previous workers, are degradation products, and therefore only *secondary* products, of the olefin–sulphur reaction. The pentasulphide $R{\cdot}S_5{\cdot}R'$ derived from *cyclo*hexene stands at about the limit of practical distillability for non-rotary molecular stills operating at 10^{-5}—10^{-6} mm. pressure and temperatures below 150°; therefore its separation from the higher-boiling residue tended always to be very incomplete, and, in consequence, the total bulk too small to permit of its satisfactory rectification. It is perhaps significant that the undistilled residue before removal of any pentasulphide had an average composition agreeing almost exactly with that required for the hexasulphide. Variation in the proportion of sulphur employed within the observed limits of $\frac{1}{8}$ to $\frac{7}{8}$ atom of sulphur per mol. of olefin affects mainly the yield, and not the nature of the sulphides obtained.

It was at once noticeable that the alkyl radicals in these polysulphides were not wholly saturated, and, indeed, the hydrogen contents of the sulphides as determined by the most careful technique of elementary analysis available usually lay but a little above * those required for the formula $C_6H_9{\cdot}S_x{\cdot}C_6H_{11}$, or alternatively those required for an equimolecular mixture of $C_6H_9{\cdot}S_x{\cdot}C_6H_9$ and $C_6H_{11}{\cdot}S_x{\cdot}C_6H_{11}$ together with (possibly) some small or large proportion of admixed $C_6H_9{\cdot}S_x{\cdot}C_6H_{11}$. In other words *the atom-ratio of hydrogen to carbon* (H/C) *in all the sulphides produced* (*in the primary reaction*) *by sulphuration was found to be identical, within the limits of analytical error, with that of the original olefin, which signified that no serious net gain or loss of hydrogen as hydrogen sulphide or thiol could have occurred to that portion of the hydrocarbon which became successfully converted into sulphides*, and hence meant that any postulation of dehydrogenation of the hydrocarbon to give hydrogen sulphide as the first necessary stage of sulphur attack must require as a corollary the complete re-addition of the hydrogen sulphide to the olefinic materials present, and must correspondingly preclude any *overall* hydrogen-enrichment of the sulphurated products at the expense of concomitantly stripped hydrocarbon molecules, but not necessarily the enrichment of individual sulphurated species (disulphides, trisulphides, etc.) at the expense of each other.

The accurate determination of total unsaturation in the partly olefinic sulphides presents a difficult practical problem which has not been satisfactorily solved: catalytic hydrogenation methods fail owing to catalyst poisoning, and all halogen addition methods which we have sought to use are invalidated owing to the high co-ordinating capacity for halogens of the combined sulphur atoms.† The determination of the distribution of unsaturation presents a still more difficult problem. At first, owing to definite analytical indications (derived from the magnitude of the hydrogen contents) that the unsaturation of the polysulphides varied appreciably within the same individual species (*i.e.*, from one sub-fraction to another), and also to the fact that a quite considerable proportion of pure saturated di*cyclo*hexyl sulphide could be isolated in the form of its methiodide from the monosulphide derived from *cyclo*hexene, it seemed likely that each species of sulphide (mono-, di-, etc.) contained some saturated material, $R_{\text{sat.}}{\cdot}S_x{\cdot}R_{\text{sat.}}$, and some dialkenyl material, $R_{|\overline{\overline{1}}}{\cdot}S_x{\cdot}R_{|\overline{\overline{1}}}$—these in equimolecular proportions—probably in addition to the " average compound " $R_{\text{sat.}}{\cdot}S_x{\cdot}R_{|\overline{\overline{1}}}$. This generalisation is probably true in respect of the sulphuration products derived from most mono-olefins, but it does not appear to be true of the sulphurated products from hydroaromatic mono-olefins because in such examples a subsidiary phenomenon seems to enter to complicate the normal course of reaction. Infra-red spectroscopic evidence ‡ shows that much of the unsatuation surviving in the sulphides from *cyclo*hexene is conjugated unsaturation, and the most likely source of this conjugation (in view of its complete absence from the synthetically derived sulphides of all olefins and polyolefins so far examined) § is dehydrogenation, doubtless produced by secondary

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* This excess doubtless merely reflects the usual tendency of hydrogen values to be rather high.

† Some progress in respect of halogen-addition methods has been made by Bloomfield (cf. *J. Soc. Chem. Ind.*, 1945, **64**, 274) since this work was carried out.

‡ We record our great indebtedness to Dr. G. B. B. M. Sutherland and Mr. N. Sheppard for their invaluable co-operation in the determination of the structure of sulphur compounds. All items of infra-red spectroscopic evidence herein depend on their observations.

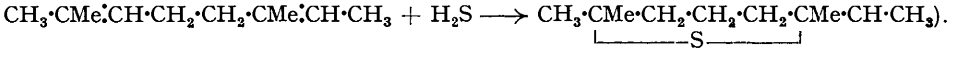
§ The possibility that resonance in groups of vinyl sulphide type (·C:C·S·) is in some degree responsible has not yet been specifically examined.

reaction. There is every reason to suspect that the superior ease of dehydrogenation of *cyclo*hexene over *cyclo*hexane is due to the susceptibility of the α-methylenic hydrogen atoms to removal (as *atoms*) by the reagent, permitting the *cyclo*hexenyl radicals so formed to achieve stabilisation by disproportionation ($2C_6H_9{*} \longrightarrow C_6H_8 + C_6H_{10}$), or by donation of a second hydrogen atom to sulphur or to $^*SH$ radicals; there is no obvious reason why the *cyclo*hexenyl groups of sulphides $R{\cdot}S_x{\cdot}R'$ should be immune from similar dehydrogenation, but of course to the extent that the unsaturation of some of the groups R and R′ is increased, that of others must ultimately disappear, so that the overall (or average) unsaturation is not quantitatively altered. There are no experimental indications that any considerable amount of *free* hydrogen sulphide (rather than $^*SH$ or $^*S_xH$) is ever produced by dehydrogenation reactions and thereafter used up again in additive reactions, although minor reactivity of this type is not unlikely.

Reaction with 1-*Methyl*cyclo*hexene*.—The reaction followed exactly similar lines to that observed for *cyclo*hexene. Only a trace of free hydrogen sulphide and no thiol was formed; also the amount of monosulphide, $R{\cdot}S{\cdot}R'$, produced was very small. That portion of the product which was distillable under high vacuum below 150° consisted of mono-, di-, tetra-, and penta-sulphides, the last being distillable only with great difficulty and hence not completely isolable from the high-boiling residue, or wholly separable from admixture with the tetrasulphide. The sulphides again agreed in composition with the general formula $R{\cdot}S_x{\cdot}R'$, the groups RR′ containing between them, on average, one double bond. Probably conjugation due to dehydrogenation appears in these sulphides (although this has not been experimentally verified), so precluding them from representation by the average formula $C_7H_{11}{\cdot}S_x{\cdot}C_7H_{13}$ or by the equivalent mixture of saturated and diolefinic forms $C_7H_{13}{\cdot}S_x{\cdot}C_7H_{13}$ and $C_7H_{11}{\cdot}S_x{\cdot}C_7H_{11}$.

Reaction with iso*Butylene*.—In this instance also there was no appreciable amount of hydrogen sulphide or thiol produced, and the lowest sulphide isolated was $R{\cdot}S_2{\cdot}R'$. This, together with the tri- and tetra-sulphide, formed almost the whole reaction product. No conjugation of the groups R and R′ was observed in this case.

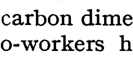
Reaction with Diolefins.—The manner of reaction of two bi-spaced olefins of the terpene group, *viz.*, dihydromyrcene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, and geraniolene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$ was next examined, the thermal treatment being conducted as before. With dihydromyrcene about two-thirds of the hydrocarbon was recovered in unsulphurated condition. Of the sulphurated products about half consisted of a mobile *monosulphide* $C_{10}H_{18}S$, which from its low boiling point, its not unpleasant smell, the zero value of its active hydrogen content, and the total absence of thiol reactivity, was clearly a cyclic sulphide. The remaining half was a red, viscous oil, easily decomposable, when heated above 140° or very slowly at 140° when no solvent or excess hydrocarbon was present; this product was wholly undistillable except at 10^{-5}—10^{-6} mm. in a molecular still, and apparently consisted of mixtures of sulphides of the type $R{\cdot}S_x{\cdot}R'$ analogous to these described above. The monosulphide readily formed a crystalline sulphonium iodide with methyl iodide and had a H/C ratio indistinguishable from that of the parent dihydromyrcene. The latter characteristic ruled out the possibility that hydrogen sulphide formed by dehydrogenation of some of the hydrocarbon molecules had added to the double bonds of other molecules to give a *saturated* cyclic product (*e.g.*,



$$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3 + H_2S \longrightarrow \underbrace{CH_3{\cdot}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{\cdot}CH{\cdot}CH_3}_{S}).$$

Indeed, observation of the infra-red spectrum showed unmistakably that the monosulphide was unsaturated, and also revealed the presence of certain characteristic olefinic groupings (see below).

Geraniolene behaved in a precisely similar manner with sulphur at 140°, the sulphurated product containing a large proportion of olefinic cyclic sulphide $C_9H_{16}S$ and a residue of mixed sulphides which appeared to be of type $R{\cdot}S_x{\cdot}R'$.

Formulation of the Sulphides. Open-chain Sulphides.—The method of linking of the sulphides derived from *cyclo*hexene, 1-methyl*cyclo*hexene, and *iso*butylene was first examined by desulphuration. The removal of sulphur by hydrogenolysis from open-chain forms $R{\cdot}S_x{\cdot}R'$ should give simple saturated hydrocarbons RH, R′H (RH_3 or $R'H_3$ if R or R′ is olefinic), whereas its removal from forms such as , showing carbon-to-carbon cross-linking, would inevitably give hydrogenated hydrocarbon dimers R–R (or $RH_2{\cdot}R$, $RH_2{\cdot}RH_2$, etc., if the sulphide is olefinic). Bougault and his co-workers had shown that sulphur can be entirely removed from a wide range of sulphur compounds by acting on them with Raney nickel containing adsorbed hydrogen; Mozingo (*J. Amer. Chem. Soc.*, 1943, **65**, 1013) had later shown that the action in the case of typical organic sulphides consisted in the severing of the C–S bonds with formation of the corresponding simple hydrocarbons: $R{\cdot}S{\cdot}R' \xrightarrow{2H_2} RH + R'H + H_2S$.

The procedure was applied to the total sulphur product from *cyclo*hexene, 1-methyl*cyclo*hexene, and *iso*butylene, and also to homogeneous monosulphides such as di*cyclo*hexyl and di*cyclo*hexenyl sulphides. In each case there remained volatile (unimolecular) hydrocarbons free from corresponding dimeric (carbon-to-carbon cross-linked) forms.

It appears, therefore, that sulphur molecules (probably chains of sulphur atoms derived by rupture of S_x rings) unite at either end with olefin molecules in virtue of the reactivity of their terminal atoms. It may tentatively be considered that such open-chained sulphur molecules will have radical ends.† In the case of the monosulphides (which are formed usually in small yield) there are two possible routes of formation: they may result from the union of single sulphur atoms (presumably $^*S^*$) with the olefins, or from the degradation of already formed polysulphides or polysulphide radicals, $R{\cdot}S_x^*$, to give RS^*. Experience has shown that when sulphur is liberated in the course of a thermal decomposition reaction (presumably in atomic condition) it is energetically reactive towards olefins, whereas elementary sulphur reacts quite slowly, even with very reactive olefins such as polyisoprenes. There is some ground, therefore, for suspecting that the small yields of monosulphides ordinarily obtained in cautiously conducted olefin–sulphur reactions may not arise from the action of monatomic sulphur. It is convenient, however, in order to simplify the argument, to assume provisionally in the following section that the reagent is monatomic biradical sulphur.

Cyclic Forms.—Owing to (1) the plurality of reaction paths open to the olefin and the sulphur reagent (having regard to the potential versatility of both), and (2) the strong possibility that cyclisation will lead to the formation of both 5- and 6- (but not 3-, 4-, and 7-) membered rings, there is little likelihood that the cyclic products formed respectively from dihydromyrcene and geraniolene will be homogeneous compounds. Efforts to separate pure or tolerably pure isomeric or structurally related forms from the two volatile sulphides—either by direct fractionation or by the formation of crystalline derivatives—proved abortive. The probability of their structural heterogeneity, however, is enhanced by the complexity of their infra-red absorption spectra in comparison with the spectra of authentic specimens of allied 6-membered saturated cyclic sulphides. The absorption curves, indeed, were in each case too complex to reveal directly the precise character of all the compounds, and for the present, necessary comparisons with corresponding 5-membered forms have had to be omitted owing to difficulties attending synthesis of the latter. But although complete interpretation of the data has not yet been possible, the deductions which have been made from a partial analysis (*q.v.*) are illuminating.

It is necessary to envisage that a radical reagent may in general attack an olefin either by replacing an α-methylenic hydrogen atom or by adding to the double bond, and it is not *a priori* impossible for the two types of reaction to occur side by side. The degree of variability to be associated with the α-methylenic (substitutive) type of reaction is mainly, but not solely (see below), that arising from the presence of two or more α-methylenic groups in the olefin undergoing attack, with the resultant possibility that attack may be initiated at more than one point in the olefinic chain. The degree of variability to be associated with the additive reaction is (for a mono-olefin) only that which could arise if the radical reagent possesses the ability to add at *either* end of the double bond. Now it has already been suggested by one of us (Farmer, *J. Soc. Chem. Ind.*, 1947, **66**, 86) that the addition of radicals and radical reagents to unsymmetrical alkylethylenes is just as strictly and universally governed by a " radical-addition " rule as is the corresponding addition of polar reagents by the well-known " polar-addition " rule of Markovnikov. Thus, whereas Br^- would always add to the alkylated carbon atom in $CHR{:}CH_2$, Br^* (and the same applies also to other radical addenda) could just as inevitably add, if it added at all, to the other carbon atom.

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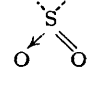
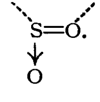
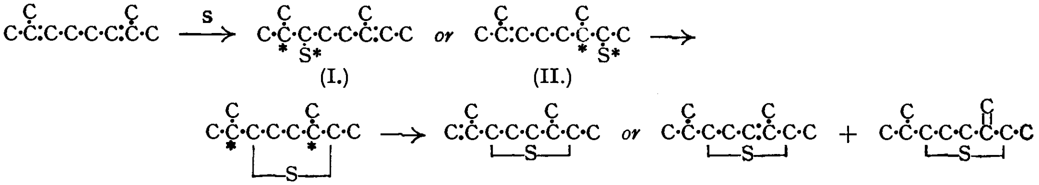
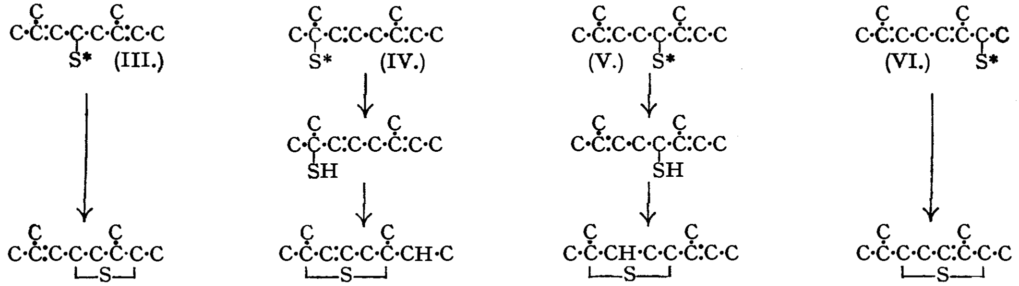
† Molecular oxygen appears to have both a biradical and an unsaturated form ($\cdot\ddot{\text{O}}{:}\ddot{\text{O}}\cdot$ and $\ddot{\text{O}}{=}\ddot{\text{O}}$), the latter of which enables it to form interpolymers with some olefins. Sulphur does not appear to form interpolymers at all and hence presumably has no unsaturated reaction form, but sulphur dioxide forms interpolymers with great ease (Staudinger and Ritzenthaler, *Ber.*, 1935, **68**, 455; Marvel *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 1815; 1935, **57**, 1691, *et seq.*) and so must be able to assume a bifunctional reaction form, presumably  or 

The approach to the determination of the structures present, and to the formulation of an adequate reaction scheme, has been greatly facilitated by Naylor's parallel study of the polar and non-polar addition of hydrogen sulphide to di-isoprenic hydrocarbons (see Part II, following paper); for the results of this study are clear-cut, since not only are the cyclic products then saturated, and so free from troublesome non-uniformity in the degree and position of unsaturation, but the unsaturation pattern of the original di-isoprene is exactly that required to give either by the polar or by the non-polar process *solely* 6-membered sulphide rings. In contrast, the additive reaction which a single sulphur atom may be expected to pursue presents the high probability that marked non-homogeneity will arise in the end-product, since the bi-radical adducts (I and II) which are probably first formed, must achieve stabilisation by hydrogen transfer (*i.e.*, probably mainly by disproportionation) in such a way that *on average* one double bond (and that bond not usually one of the original two) is retained and one lost; to some doubtless minor extent, however, the disproportionation may well yield an equimolecular mixture of the corresponding diolefinic and fully saturated sulphides.[†] If, however, reaction follows the α-methylenic course, attack by the reagent is likely to be confined almost entirely to the two α-methylene groups between the two double bonds, leaving those in the methyl groups intact; but owing to the capacity for resonance in any radical propene system that is formed when an α-methylenic hydrogen atom is detached (*C·C:C $\rightleftharpoons$ C:C·C*) there will be four potential ways (III—VI) in which reaction may be initiated but only two of these, *viz.*, (III) and (VI), will lead to the successful production of cyclic forms if the radical-addition rule is to be obeyed and only 5- and 6-membered rings are capable of formation.





There is, however, a further possibility for the formation of cyclic sulphides which cannot be neglected, *viz.*, that which arises if the active thiol centres in (III—VI) become stabilised by capture of the hydrogen atoms (see preceding footnote) and the resulting ·SH groups thereafter add themselves by polar mechanism (wherever the Markovnikov rule and the usual limitation of ring size jointly permit) to the more remote double bond. This polar type of addition would be likely to occur readily owing to the strong catalytic action of the free sulphur present (see Part II).[‡] Of the four α-methylenic sulphuro-forms, however, only two, (IV) and (V), would yield cyclic sulphides (*viz.*, VII and VIII); the olefinic thiols corresponding to (III) and (VI), if formed at all, would survive. Actually, the amount of such thiol that survived as determined

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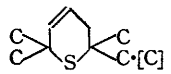
[†] The path taken by the disproportionation probably depends on the incidence of intra- and intermolecular hydrogen displacements respectively, the former leading exclusively to the product of average unsaturation (*i.e.*, to the mono-olefinic cyclic sulphide) and the latter probably largely to the mixture of saturated and diolefinic forms. To the extent that the addition of the sulphur to one double bond is completed (*i.e.*, the first-formed radical sulphuro-product becomes stabilised by hydrogen rejection *before* that to the other double bond occurs), to that same extent the discarded hydrogen atoms are likely to add to the ·S* groups giving the thiols corresponding to (III)—(VI).

[‡] Since polar and non-polar additions of hydrogen bromide (or hydrogen sulphide) to olefins occur readily side by side, there is no reason to suppose that the two kinds of addition may not occur together in this case.

by usual methods was extremely small, but was possibly slightly underestimated; only later did the very efficient analytical and separative method used in Part II become available. Thus, altogether, the cyclic sulphides likely to be formed from dihydromyrcene by α-methylenic initiation are (VII), (VIII), (IX), and (X); and those from geraniolene precisely the same forms minus the carbo-group (CH_3) enclosed in square brackets. Correspondingly those likely to be formed by additive initiation are (X) and (XI), with possibly a very minor amount of (XII).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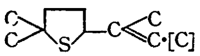
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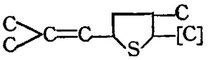
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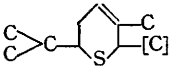
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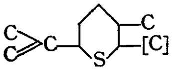
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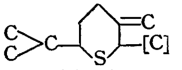

(XII.)

Now the infra-red absorption data show that, as regards the 6-membered forms from both dihydromyrcene and geraniolene, the skeletal pattern depicted in (VII) preponderates over that in (X); also it is plain that one or more of the isomers present contains a methyleno-grouping $CH_2{:}CRR'$ such as occurs in (XI) and in the minor isomer (XII). Hence α-methylenic initiation of the sulphuration reaction undoubtedly occurs to an important extent and may well greatly exceed additive initiation. It is of especial interest that the change from the $CRR'{:}CHR''$ structure occurring in the olefinic units of the di-isoprene to the $CHR{:}CHR'$ structure of the derived cyclic (and doubtless also of the cross-linked) sulphuro-product, as seen in (VII), with all that it implies in the way of α-methylenic initiating attack at *a* in $\cdot CH_2\cdot CMe{:}CH{-}\underset{a}{C}H_2\cdot$ as discussed above, is encountered again in the sulphuration of rubber, since Sutherland and Sheppard's infra-red spectroscopic data (private communication) show that the progress of this change keeps pace with increase in the uptake of sulphur.

It is to be noted that no products of the episulphide (thioepoxide) type have been discoverable in the fore-runs of the sulphurated mono-olefins or in the cyclic monosulphide fractions from dihydromyrcene and geraniolene; and indeed, no adequately substantiated method of obtaining such compounds save the usual one of reaction between sulphide and suitable halogeno-compounds appears yet to be known. The chemical behaviour of thioepoxy*cyclo*hexane, a typical compound of this group, differs considerably from that of the open-chain and cyclic monosulphides discussed above.

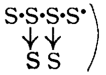
Nature of Sulphur Vulcanisation and the Stability of Sulphurated Products.—It has been shown by one of us (Farmer and Michael, *J.*, **1942**, 513) that decomposing peroxides effectively promote the carbon-to-carbon cross-linking (α-methylenically initiated) of olefinic materials, and also of ketonic and carboxylated materials (cf. Farmer, "Advances in Colloid Science," 1946, II, 316). Decomposing diazo-compounds often have a similar effect, and with both classes of reagent the process follows a radical mechanism which is irreversible except in so far as the cross-linked products become broken down (and even then not usually into their exact precursors) when they are heated to the point of thermal breakdown of the weakest C–C bonds (>250°). With regard to sulphur vulcanisation, the only cross-linking which has been discoverable in the present investigation is that brought about by the linking of the hydrocarbon chains through sulphur atoms or groups of sulphur atoms. The concomitant formation of monosulphide rings in the case of di-isoprenes is to be regarded as amounting to *intra*molecular cross-linking, the different olefinic units becoming joined being in the same instead of in different molecules; such intramolecular linking is of course liable to take place wherever the reactant olefin molecules contain two or more suitably-spaced double bonds. But to the extent that cyclising sulphuration occurs at the expense of true cross-linking, the ingoing sulphur is apparently not used effectively (or at least not in the most effective way) for the conferring of " vulcanised " properties. The sulphur-vulcanisates, as a class, whether formed from short-chained olefins or high-molecular polyolefins, differ greatly from the carbon-to-carbon cross-linked vulcanisates in being highly susceptible to thermal treatment at temperatures but little above (or, possibly, where heating is very unduly prolonged, even *at*) the vulcanisation temperature. This relative instability (thermolability) appears to be a property of considerable moment in connection with the technology of natural and synthetic rubbers, causing as it does the replacement of some primary structures by secondary ones. The two structural features concerned in this instability are the C–S bonds and (in the case of *poly*sulphides) the polysulphide chains.

The Stability of C–S *Bonds.*—The susceptibility of C–S bonds to thermal degradation is reserved for future study. In general, the strength of the bonds as it occurs in cross-linked structures is likely to vary very appreciably with the nature of the hydrocarbon chains in the immediate vicinity of the bond: indeed, having regard to the foregoing results, distinction may be made between three types of monosulphide bridge, *viz.*, (*a*) the diallylic type, $C{=}C{-}C{-}S{-}C{-}C{=}C$, (*b*) the alkyl-allyl type $C{-}C{-}C{-}S{-}C{-}C{=}C$, and (*c*) the dialkyl type, $C{-}C{-}C{-}S{-}C{-}C{-}C$. As regards the stability of the C–S bond to *chemical* reagents, it has previously been suggested by one of us that the well-known non-uniform action of organic bases on the sulphur vulcanisates of rubber is probably connected with differences in structure near the sulphur bridge; in the present paper, however, attention is confined to evidence concerning the breaking of C–S bonds (*a*) under the reducing action of sodium in alcohol, and (*b*) by action of methyl iodide.

Experiment showed that completely saturated sulphides such as di-*n*-propyl sulphide and di-*n*-butyl sulphide remained unattacked by the reducing agent, whereas dialkenyl sulphides such as diallyl, dicrotyl, and di*cyclo*hex-2-enyl sulphides broke down readily to give approximately equimolecular amounts of hydrogen sulphide and thiol, *e.g.*,

$$[CH_2{:}CH{\cdot}CH_2]_2S \xrightarrow{H} CH_2{:}CH{\cdot}CH_3 + CH_2{:}CH{\cdot}CH_2{\cdot}SH, \textit{ and } 2CH_2{:}CH{\cdot}CH_3 + H_2S.$$

Mixed sulphides, of which two (*propyl allyl sulphide* and cyclo*hexyl* cyclo*hexenyl* sulphide) were tested, gave an intermediate result, passing to the corresponding thiol but giving no hydrogen sulphide. Thus the C–S bond seems to be attacked by the reducing agent only when the carbon atom is in the α-position to a double bond, or in other words the sulphur atom can be reductively detached from α-methylene groups to which it is linked, but not from saturated carbon chains. The cyclic sulphides from dihydromyrcene and geraniolene gave, as would be expected from the constitutions assigned above, much thiol but no hydrogen sulphide, but reaction was considerably more sluggish, presumably on account of the alkyl substitution at each of the α-methylene groups. For comparison, a compound of the olefin thioepoxide group, *viz.*, thioepoxy*cyclo*hexane, was tested: this, in spite of the saturated chain attached on either side to the sulphur atom, underwent ready reduction to a mixture of thiol and hydrogen sulphide.

Instability of Polysulphide Chains.—The ability of sulphur atoms to become linked in chains or groups, and for elementary sulphur to exist normally in closed chains of eight, six, or possibly fewer atoms is commonly regarded as an expression of the strong co-ordinating power of sulphur, and hence there is some expectation that branching of sulphur chains due to co-ordination (*e.g.*,  $\begin{array}{l} S{\cdot}S{\cdot}S{\cdot}S{\cdot} \\ \downarrow\,\downarrow \\ S\;S \end{array}$) may frequently occur. The high-molecular polysulphides formed by the polymeric interaction of organic dihalides and sodium tetrasulphide (Patrick, *Trans. Faraday Soc.*, 1936, **32**, 347) are reported to contain co-ordinated sulphur atoms in their polysulphide groups, since a proportion of the sulphur can be easily removed by caustic alkali. It is reasonable to suppose that the alleged co-ordinated structure is derived directly from the tetrasulphide reagent, and that corresponding syntheses starting out from normal-chained polysulpho-reagents will yield unco-ordinated polysulphides which will not be "stripped" by caustic alkali (cf. Patrick, *loc. cit.*) or by sodium sulphite (cf. Parker, *India Rubber J.*, 1945, **108**, 387). A study of polysulphide constitution and instability will appear in a later part of this series; therefore it suffices now to point out that in our experiments the removal of sulphur by caustic alkali or sodium sulphite succeeds with the above-described products of the olefin–sulphur reaction *only* to the extent of a few units %, suggesting that the sulphur chains are almost wholly unbranched; in contrast to this, however, the diethyl tetrasulphide derived from sulphur monochloride, usually believed to be Cl·S·S·Cl, and ethylthiol ($Cl{\cdot}S_2{\cdot}Cl + 2Et{\cdot}SH \longrightarrow Et{\cdot}S{\cdot}S_2{\cdot}S{\cdot}Et + 2HCl$), as also that derived by the interaction of sodium tetrasulphide which according to the foregoing indications is branched, and ethyl iodide, surrenders nearly half its sulphur to the stripping agent. Hence there is no certainty that sulphur removed by mild stripping agents is necessarily co-ordinated sulphur, or that straight sulphur chains cannot often be ruptured and deprived of part of their sulphur by the same means.

All di- and poly-sulphides formed in the olefin–sulphur reaction decompose progressively at temperatures above 140° (especially from 160° upwards) into hydrogen sulphide, thiol, and monosulphide, but when temperatures above 140° are avoided in the working up of the products comparatively little monosulphide (with some olefins, none at all) and only traces of hydrogen sulphide are formed. Therefore the formation of a *large* proportion of monosulphide in any olefin–sulphur reaction is fairly safely to be attributed to secondary action, *i.e.*, to thermal decomposition of primary polysulphides due to too long heating or too high temperatures; apparently, however, some monosulphide is produced as a primary product, and there is no evidence as yet to suggest that the cyclic monosulphides from the di-isoprenes are other than primary products, although thermal decomposition of polysulphides may well be able to produce additional amounts. The amount of thiol formed in the thermal decomposition of the polysulphides from *cyclo*hexene (as also those from 1-methyl*cyclo*hexene) is comparatively large, being formed apparently by progressive breaking of the S–S–S– chains, followed by capture of hydrogen atoms from surrounding olefinic molecules ($R{-}S{-}\vdots{-}S{-}S{-}S{-}\vdots{-}SR' \longrightarrow R{-}S^*$ or $R'{-}S^* \longrightarrow R{-}SH$ or $R'{-}SH$). Experiment, indeed, showed that when a polysulphide mixture was distilled above the decomposition temperature, the later distillate fractions showed a H/C ratio progresively smaller and smaller until finally a solid residue containing 39·5% of sulphur but only 3·75% of hydrogen (H/C = 6 : 4·75) was left. The thiol formed by degradation appears always to be partly olefinic. Disproportionation of the sulphur content doubtless normally accompanies thiol formation when the sulphur chain is severed; Hinsberg (*Ber.*, 1910, **43**, 1874) early observed that aromatic disulphides yielded monosulphide and trisulphide as well as some thiol; and other similar instances are on record.

The Sulphur Reagent and the Initiation of Reaction.—It is provisionally concluded from the foregoing that the ordinary reaction form of sulphur in the rather slow sulphur–olefin reactions is the open, radical-terminated sulphur chain, and consequently that in the formation of the cyclic monosulphides the first step may still possibly consist in the union of one end of such sulphur chain with an olefin molecule, later to be followed by rupture of the sulphur chain ($>C{\cdot}S{\cdot}\vdots S{\cdot}S{\cdot}S{-} \longrightarrow >C{\cdot}S{-} + {-}S{\cdot}S{\cdot}S{-}$). The preceding results provide some ground for believing that α-methylenic initiating attack by the sulphur reagent predominates over additive attack. A difficulty, however, arises in connexion with the latter view, which is left for future resolution, *viz.*, that there is a very sharp contrast between the relatively facile carbon-to-carbon molecule-linking action of peroxidic oxygen, *i.e.*, of the free radicals such as *OH derived from decomposing peroxides, ($2C_6H_{10} + 2{}^*OH \longrightarrow C_6H_9{\cdot}C_6H_9 + 2H_2O$) and the inefficient, but not unknown, similar cross-linking action of sulphur or sulphuro-radicals. This seems to suggest that the appearance of radical centres on α-methylenic carbon atoms either occurs relatively rarely in sulphur–olefin reactions or else such centres do not ordinarily get beyond the influence of the reacting sulphur.

EXPERIMENTAL.

(Analyses are by Dr. W. T. Chambers and Miss H. Rhodes.)

Action of Sulphur on cyclo*Hexene.*—*cyclo*Hexene (88 g.) and sulphur (25 g.) were heated together in a rotating steel autoclave for *ca.* 5 hours. A portion of the liquid product was shaken repeatedly with cold dilute potassium hydroxide solution, and the combined washings acidified with hydrochloric acid and then extracted with ether. The ethereal extract gave no appreciable residue (a smell only) of thiol on evaporation; therefore the total neutral product after being carefully freed from the unchanged *cyclo*hexene by distillation was directly fractionated. The dark brown viscous liquid was first heated at 0·1 mm. pressure (the heating bath being kept below 140°), whereupon a nearly colourless oil (4 g.), b. p. 70—100°, distilled. This was refractionated, giving (i) a monosulphide, b. p. 70° (*ca.* 0·5 g.) and (ii) a *disulphide* of b. p. 106° (*ca.* 3·4 g.). The monosulphide was a mixture of unsaturated and saturated forms (Found: C, 72·9; H, 10·5; S, 16·4; H : C = 10·2 : 6. Calc. for $C_{12}H_{20}S$: C, 73·4; H, 10·3; S, 16·35%; H : C = 10 : 6. Cal. for $C_{12}H_{22}S$: C, 76·65; H, 11·15; S, 16·2%; H : C = 11 : 6), containing some di*cyclo*hexyl sulphide since it gave with methyl iodide a poor yield of di*cyclo*hexylmethylsulphonium iodide, m. p. 110·5° (mixed m. p. with authentic specimen derived from pure di*cyclo*hexyl sulphide, 110·5°) Meyer and Hohenemser (*loc. cit.*) had shown that less cautious heating of the total sulphuration product gave a much higher yield than that here obtained of a comparable monosulphide which was thought to consist wholly or mainly of di*cyclo*hexyl sulphide, since it gave with methyl iodide the above mentioned sulphonium iodide, m. p. 110·5°. The disulphide, also, was partly unsaturated (Found: C, 63·4; H, 9·05; S, 27·5; H : C = 10·5 : 6. $C_{12}H_{20}S_2$ requires C, 63·1; H, 8·8; S, 28·05%. $C_{12}H_{22}S_2$ requires C, 62·6; H, 9·65; S, 27·8%).

The visocus residue in the still was transferred to a "molecular" still and further fractionated. In this operation a Waterman (vertical-type) still gave poor results owing to unavoidable "channeling" of the distilland on the heating surface due to low wetting-capacity for glass: hence a pot-still operating at *ca.* 10^{-5} mm. was used in preference. Numerous fractions of increasing sulphur content were successively collected, including two fractions both showing unsaturation, consisting respectively of a *tri-* and a *tetra-sulphide*. The trisulphide, $n_D^{18°}$ 1·5884, was a thick, pale yellow liquid (Found: C, 55·6; H, 7·95; S, 36·4; H : C = 10·2 : 6. $C_{12}H_{20}S_3$ requires C, 55·3; H, 7·75; S, 36·95%. $C_{12}H_{22}S_3$ requires C, 54·9; H, 8·45; S, 36·65%), and the tetrasulphide, a still more viscous yellow liquid (Found: C, 49·7; H, 6·95; S, 43·15; H : C = 10·0 : 6. $C_{12}H_{20}S_4$ requires C, 49·3; H, 6·9; S, 43·8%); the latter had $n_D^{18°}$ 1·6130, $d_{4°}^{18°}$ 1·209, $[R_L]_D$ 84·20 (Calc. for $C_6H_{11}{\cdot}S_4{\cdot}C_6H_9|_1$, using Twiss's refractivity value for the sulphur of disulphides: 85·15).

The final residue in the still (*ca.* 34 g.) was a very dark, viscous liquid, varying a little in composition from experiment to experiment. Typical analytical values were: C, 40·95; H, 5·75; S, 53·45; H : C = 10·05 : 6. (Calc. for $C_{12}H_{20}S_6$: C, 40·45; H, 5·65; S, 53·9%). The separation of a pentasulphide from this residue by further distillation could be effected only with difficulty and incompletely. One such crude product, a reddish oil, had S, 52·9% (Calc.: S, 53·9%).

The recovered *cyclo*hexene was examined spectroscopically in U.V. light, by Dr. H. P. Koch. Less than 1% of benzene and an almost negligible amount of *cyclo*hexadiene were found to be present.

Several further reactions between *cyclo*hexene and sulphur were carried out as above, diminishing proportions of sulphur being used (down to 0·18 atom per mol.). The sulphurated products were in all cases quantitatively similar to the foregoing, but the total yield diminished with reduction in the amount of sulphur employed.

Action of Sulphur on 1-*Methyl*cyclo*hexene*.—The hydrocarbon (30 g.) and sulphur (7 g.) were heated in a sealed tube at 140—145° for *ca.* 6 hrs. The unchanged hydrocarbon (15 g.) was distilled off through a column, leaving a rather thick brown liquid, from a sample of which repeated vigorous agitation with aqueous sodium hydroxide extracted no thiol. Distillation at 0·1 mm. (bath below 145°) gave only a very small amount (too small for refractionation) of crude *monosulphide*, contaminated with hydrocarbon (Found : S, 12·2. $C_{14}H_{24}S$ requires S, 14·3%). Continuation of the distillation at 10^{-5} mm. gave a succession of fractions of increasing viscosity and deepening yellow colour corresponding respectively to *disulphide* $C_7H_{11}\cdot S_2\cdot C_7H_{13}$ (Found : C, 65·0; H, 9·55; S, 25·3; H : C = 12·25 : 7. $C_{14}H_{24}S_2$ requires C, 65·6; H, 9·45; S, 25·0%), *trisulphide*, $C_7H_{11}\cdot S_3\cdot C_7H_{13}$ (Found : C, 57·85; H, 8·4; S, 34·0; H : C = 12·1 : 7. $C_{14}H_{24}S_3$ requires C, 58·25; H, 8·4; S, 33·35%), and a *tetrasulphide*, $C_7H_{11}\cdot S_4\cdot C_7H_{13}$ (Found: C, 52·25; H, 7·7; S, 39·85%; H : C = 12·3 : 7. $C_{14}H_{24}S_4$ requires C, 52·45; H, 7·55; S, 40·0%). The *pentasulphide*, which distilled with great difficulty, was not completely isolated, or wholly freed from residual tetrasulphide. The crude fraction formed a dark reddish oil (Found : C, 49·6; H, 7·5; S, 43·1. $C_{14}H_{24}S_5$ requires C, 47·6; H, 6·85; S, 43·1%).

Action of Sulphur on iso*Butylene*.—The liquid hydrocarbon (56 g.; 1 g.-mol.) was introduced at −50° into a steel autoclave which contained sulphur (35 g.; 1·1 g.-mol.). The sealed autoclave was heated at 140—150° for 14 hrs., then strongly cooled and opened. A sample of the liquid contents was tested at once for thiol by Bell and Agruss's test (*Ind. Eng. Chem. Anal.*, 1941, **13**, 297); no significant proportion was present. The unreacted *iso*butylene was allowed to evaporate, and the liquid residue (53·8 g.) distilled. The first distillate was a red liquid, b. p. 80°/12 mm. (21·8 g.), and the second a dark red rather thick liquid, b. p. 90°/0·5 mm.; there remained a dark red very viscous liquid in the still (*ca.* 14 g.). The first two distillates were separately fractionated and the products refractioned. Although these two stages of rectification did not result in perfect segregation of the individual polysulphides, an approximate separation into *di-*, *tri-*, and *tetra-sulphides* was achieved. The various fractions were yellow, reddish yellow, red and dark red liquids of increasing viscosity. The following analytical data for the fractions (*a*)—(*k*) were obtained :—

Fraction, b. p./0·5 mm.	Found, %. C.	H.	S.	*n*.	H : C.	Sulphide.
(*a*) Forerun *						
(*b*) 38°	54·5	10·0	34·95	$n_D^{15°}$ 1·5005	8·75 : 4	*Di-*
(*c*) 38—39°	52·95	9·6	37·0	$n_D^{15°}$ 1·5070	8·7 : 4	
(*d*) 39—40°						
(*e*) 40—44°	—	—	44·5	$n_D^{19·5°}$ 1·5292	—	
(*f*) 44—51°	—	—	44·7	$n_D^{19·5°}$ 1·5330	—	—
(*g*) 51—60°	44·65	8·2	45·4	$n_D^{19·5°}$ 1·5407	8·8 : 4	*Tri-*
(*h*) 60—70°	43·65	7·65	47·6	$n_D^{19·5°}$ 1·5620	8·4 : 4	—
(*i*) 70—80°	—	—	—	—	—	—
(*j*) 80—90°	38·95	6·75	53·6	—	8·26 : 4	*Tetra-*
(*k*) Viscous residue	41·3	6·55	51·6	—	7·56 : 4	—

* ($C_8H_{16}S_2$ requires C, 54·5; H, 9·1; S, 36·35%; $C_8H_{16}S_3$ requires C, 46·1; H, 7·7; S, 46·1%; $C_8H_{16}S_4$ requires C, 40·0; H, 6·75; S, 53·3%.)

It is seen that no definite monosulphide fraction could be isolated and that the ultimate very viscous residue (although doubtless very heterogeneous, and probably containing *inter alia* some triolefinic sulphides derived by double cross-linking) approximated in average composition to tetrasulphide.

Action of Sulphur on Dihydromyrcene.—The hydrocarbon (60 g.) and sulphur (6 g.) were heated at 140° for about 5 hours in a steel rotating autoclave in an atmosphere of nitrogen. The product was a dark red, somewhat viscous liquid, from which unused hydrocarbon (*ca.* 41 g.) was distilled through a fractionating column at 15 mm. pressure (Found : C, 85·85; H, 12·95; H : C = 18·1 : 10. Calc. for $C_{10}H_{18}$: C, 86·85; H, 6·65%).

About half the remaining liquid (10 g.), which yielded no significant thiol fraction when thoroughly extracted with sodium hydroxide solution, was volatile at 15 mm. (b. p. 90—92°; $n_D^{17°}$ 1·4966). This product, a *monosulphide* of dihydromyrcene, could not be completely freed from the last traces of hydrocarbon by repeated fractionation under a good column; the sulphur content was accordingly unavoidably low (Found : C, 70·85; H, 10·7; S, 18·4; active H, 0·02. $C_{10}H_{18}S$ requires C, 70·5; H, 10·65; S, 18·85; active H, 0·0%). This monosulphide was necessarily of cyclic constitution but improbably structurally homogeneous (see p. 1523); it gave (but only in part) with methyl iodide a *methiodide*, m. p. 130° (decomp.) (Found : S, 10·0; I, 40·5. $C_{11}H_{21}SI$ requires S, 10·25; I, 40·65%).

The undistilled sulphurated residue (*ca.* 13·5 g.) was a very viscous, dark red oil, easily soluble in hydrocarbons, carbon disulphide, and ethyl alcohol. A separation of this product into two roughly equal parts was effected by extracting it with methyl alcohol. These parts, although fairly reproducible as regards elementary composition, were probably both mixtures of sulphides, since their analyses corresponded with no definite compound. The insoluble fractions obtained in successive separations were dark brown, viscous oils (Found : S, 30·2; 28·1, 28·55%), and the corresponding soluble fractions reddish-brown oils (Found : S, 25·6, 25·1, 24·6%). These materials possessed the same general characteristics as the polysulphides from the simple olefins.

Action of Sulphur on Geraniolene.—The geraniolene (b. p. 109—111°/12 mm.) was prepared from commercial citral, which was first purified by conversion into the corresponding bisulphite compound (see Hibbert and Cannon, *J. Amer. Chem. Soc.*, 1942, **46**, 119), then oxidised to geranic acid (b. p. 118—120°/0·1 mm.; $n_D^{20°}$ 1·4880) by means of silver oxide (see Bernhauer and Forster, *J. pr. Chem.*, 1936, **147**, 199), and finally decarboxylated by heating it at *ca.* 260° in a stream of nitrogen. The crude hydrocarbon, mixed with a little geranic acid, distilled during the decomposition. Several batches of hydrocarbon were united and rectified. The final product was colourless liquid, b. p. 35—36°/15 mm., $n_D^{19°}$ 1·4410.

The hydrocarbon (72 g.) was heated with sulphur (7·0 g.) in a steel rotating autoclave for 5 hrs. at 140°. The crude product yielded no thiol fraction when thoroughly extracted with sodium hydroxide solution; it contained, however, much unconsumed hydrocarbon (about ⅘ of original bulk), which was recovered by distillation.

About half the liquid residue (*ca.* 14 g.) was distillable at 12 mm. pressure, so giving a colourless, sweet-smelling liquid similar to that obtained from dihydromyrcene and sulphur. This product, $n_D^{16°}$ 1·4840, like the dihydromyrcene derivative, retained obstinately in spite of repeated refractionations traces of hydrocarbon. In consequence the sulphur content was invariably slightly low. It boiled at 65·5—66°/12 mm. (Found: C, 69·5; H, 10·5; S, 19·9; active H, 0·02. $C_9H_{16}S$ requires C, 69·2; H, 10·3; S, 20·5; active H, 0·0%).

Desulphuration of Polysulphides.—The method of desulphuration devised by Mozingo *et al.* (*loc. cit.*), employing Raney nickel powder prepared in the recommended way, was followed. The sample of nickel used evolved, on test, 116 c.c. of hydrogen per g. on being heated in butyl phthalate suspension at 220°. The sulphur compound (*ca.* 6 g.), dissolved in a little freshly-distilled *cyclo*hexane, was dropped into a layer of freshly-distilled *cyclo*hexane which acted as covering for the pyrophoric nickel (*ca.* 120 g.). Minute bubbles of gas were liberated immediately the sulphide was added. Gentle refluxing of the mixture for 3 hours completed the reaction, whereupon the solvent was removed by careful decantation, the nickel was extracted several times by boiling *cyclo*hexane, and the solvent distilled from the united *cyclo*hexane liquors through a column. The sulphides so treated were di*cyclo*hexenyl sulphide (see below), and specimens of the total sulphuration products (freed from unconsumed hydrocarbon) derived from *cyclo*hexene, 1-methylcyclohexane and *iso*butylene. In no case did any high-boiling hydrocarbon (representing a di- or poly-molecular derivative of the olefin originally sulphurated) or any sulphide remain.

Synthesis of Sulphides, Polysulphides, etc.—(1) 3 : 3′-*Di*cyclo*hexenyl sulphide.* *N*-Bromosuccinimide (73·2 g.), prepared by the method of Ziegler *et al.* (*Annalen*, 1942, **551**, 80), and *cyclo*hexene (206 c.c.) were gently refluxed for 20 mins. in pure carbon tetrachloride (300 c.c.) in the presence of a trace of benzoyl peroxide. Succinimide, which was insoluble in the tetrachloride, was gradually precipitated and was finally filtered off. The solvent was distilled off through a column and the residue fractionated. About 40 g. of almost colourless 3-bromo*cyclo*hexene, b. p. 60—61°/15 mm., $n_D^{22°}$ 1·5395, were collected (Found: C, 44·85; H, 5·7; Br, 49·3. Calc. for C_6H_9Br: C, 44·75; H, 5·65; Br, 49·6%).

3-Bromo*cyclo*hexene (12 g.), powdered sodium sulphide (5 g.), and alcohol (15 c.c.) were sealed in a Carius tube and heated to 100° for 4 hrs. The liquid in the cooled tube was filtered, diluted with ether, washed with water, dried (K_2CO_3), and the ether distilled. The residue, when distilled at *ca.* 0·1 mm. pressure gave about 4·5 g. of a colourless liquid, b. p. 81—82°, $n_D^{25°}$ 1·5506, of not unpleasant smell. This was 3 : 3′-*di*cyclo*hexenyl sulphide* (Found: C, 74·15; H, 9·45; S, 16·35. $C_{12}H_{18}S$ requires C, 74·2; H, 9·35; S, 16·35%).

(2) cyclo*Hexyl* cyclo*hexenyl sulphide.* This was formed by the action of lead *cyclo*hexyl mercaptide on 3-bromo*cyclo*hexene. *cyclo*Hexanethiol (20 g.), prepared by the hydrolysis of *cyclo*hexyl thiolacetate with alcoholic potassium hydroxide (Cunneen, *J.*, 1947, 134), was converted into its lead salt by shaking it for some hours in a stoppered vessel with excess of aqueous lead acetate. The precipitated yellow mercaptide was filtered off, well washed, dried at reduced pressure, and then suspended in alcohol (4000 c.c.). To the suspension was added 3-bromo*cyclo*hexene (29 g.), and the whole refluxed for 1 hr. on a water-bath. After filtration, most of the alcohol was distilled off through a column, and the concentrated alcoholic residue poured into water and extracted with ether. The extract was washed with water, dried ($CaCl_2$), and distilled. Much unchanged thiol passed over first, and then a colourless liquid, b. p. 69—70°/0·1 mm., $n_D^{19°}$ 1·5317, of not unpleasant smell. The latter was cyclo*hexyl* cyclo*hexenyl sulphide* (Found: C, 73·35; H, 10·2; S, 16·15. $C_{12}H_{20}S$ requires C, 73·4; H, 10·25; S, 16·3%).

(3) *Propyl allyl sulphide.* *n*-Propanethiol (45 g.) was converted into its lead salt as above, and the dried salt suspended in alcohol. To the suspension allyl bromide (70 g.) was added with shaking, and the whole refluxed for 1 hr. The resulting liquor was filtered from insoluble lead salts, poured into water, and extracted with ether. The extract was washed with water, dried ($CaCl_2$), and distilled at atmospheric pressure. The distillate (30 g.), a colourless mobile liquid, b. p. 138—140°/755 mm., was *propyl allyl sulphide* (Found: C, 61·9; H, 10·4; S, 27·7. $C_6H_{12}S$ requires C, 62·0; H, 10·4; S, 27·55%).

(4) cyclo*Hexene thioepoxide* (*episulphide*). This was obtained by the interaction of 1-chloro-2-thiocyano*cyclo*hexane and sodium sulphide ($C_6H_{10}Cl\cdot SCN + Na_2S \longrightarrow C_6H_{10} > S + NaCl + NaSCN$). Lead thiocyanate (235 g.) was dried, placed in a 1-l. flask, and covered with dry carbon tetrachloride (600 c.c.) to which *cyclo*hexene (49 g.) had been added. The mixture was thoroughly stirred while phenyl iododichloride (153 g.) was added in small amounts during about 45 mins., and thereafter for 1 hr. The product was then filtered from insoluble lead salts, shaken with sodium thiosulphate solution to remove free dithiocyanogen, and washed as well as possible with water (the formation of emulsions gave trouble). The carbon tetrachloride solution was dried ($CaCl_2$), filtered from polythiocyanogen, and distilled. The solvent and any iodobenzene formed in the reaction were removed at reduced pressure; the residue, consisting of 1-*chloro*-2-*thiocyano*cyclo*hexane*, distilled at 90—92°/0·1 mm. as a colourless liquid, after a forerun of 3 g. had been rejected (Found: C, 47·85; H, 5·8; N, 8·15; S, 18·3; Cl, 19·95. $C_7H_{10}NClS$ requires C, 47·85; H, 5·75; N, 8·0; S, 18·2; Cl, 20·2%); $n_D^{18.5°}$ 1·5284, $[R_L]_D$ 44·86.

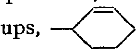
The chlorothiocyano*cyclo*hexane (31 g.) was dissolved in absolute alcohol (120 c.c.), and powdered sodium sulphide (25 g.) added. The mixture, contained in a 250-c.c. flask, was thoroughly stirred and refluxed on a water-bath for 2 hours. The cooled product was poured into water and extracted several times with ether. The extract was dried (K_2CO_3), filtered, and the solvent distilled. The residue on distillation at 15 mm. pressure gave cyclo*hexene thioepoxide* as a colourless mobile oil of distinctive odour, b. p. 56—57°, $n_D^{18°}$ 1·5350 (Found : C, 63·05; H, 8·85; S, 27·95. $C_6H_{10}S$ requires C, 63·1; H, 8·8; S, 28·05%).

(5) *Diethyl tetrasulphide.* Sodium tetrasulphide (23 g.), prepared by the method of Rule and Thomas (*J.*, 1914, **105**, 177), freshly-distilled ethyl iodide (60 g.), and absolute alcohol (90 c.c.) were refluxed on a water-bath for 2 hours in a slow stream of nitrogen. The product, when cool, was poured into water, and the precipitated oil extracted with benzene. The extract was dried (K_2CO_3), and the benzene distilled off. The oily residue, on distillation at 0·1 mm., passed over mainly at 43—45°, giving an evil-smelling, yellow oil, b. p. 43—45°, $n_D^{19°}$ 1·6105. This was undoubtedly slightly impure diethyl tetrasulphide (Found ; S, 67·4. Calc. for $C_4H_{10}S_4$: S, 68·8%), which Riding and Thomas (J., 1923, **123**, 3271; 1924, **125**, 2463), probably owing to the technique adopted, failed to isolate after carrying out the same reaction. A small forerun and a residue, obtained as by-products, may well have represented the corresponding di- and penta-sulphide which were reported by Riding and Thomas to be formed. Comparison of the product with that obtained by the action of sulphur monochloride on ethanethiol (cf. Chakravarti, *J.*, 1923, **123**, 966), including spectroscopic examination in U.V. light by Dr. H. P. Koch, disclosed no essential difference between the two, although the latter appears to be freer from impurities (see Part IV).

(6) The following thio-compounds required for comparison with products derived by interaction of olefins and sulphur, and for infra-red spectroscopic observations, were synthesised by methods fully described in the literature : Thiols, ethyl, *n*-butyl, and *cyclo*hexyl; sulphides, di-*n*-propyl, di-*n*-butyl, diallyl, dicrotyl; disulphides, di-*n*-butyl, dibenzyl.

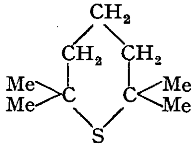
Infra-red Spectra.—The following report on the characteristics of thio-compounds has been furnished by Dr. G. B. B. M. Sutherland and Mr. N. Sheppard.

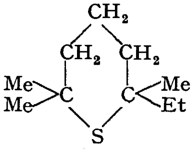
(1) *The Products of the sulphur-*cyclo*hexene reaction.* The infra-red spectra of *cyclo*hexanethiol, di*cyclo*hexyl sulphide, 3 : 3′-di*cyclo*hexenyl sulphide, and *cyclo*hexene episulphide were compared with a series of ten fractions of the reaction products.

In no case was *cyclo*hexene episulphide detectable in the reaction products, and only one of the " monosulphide " fractions showed the presence of *cyclo*hex-2-enyl groups,  . In most cases the strong bands in the spectra were nearly all those of *cyclo*hexyl groups, showing that such saturated groups predominated, but in addition every sample showed " unsaturation " bands due to C=C valency vibrations between 1590 and 1600 cm.$^{-1}$, which are in the position generally associated with unsaturation of a conjugated type. No other olefinic groups were detected.

(2) *The reaction products of sulphur with geraniolene and dihydromyrcene.* The infra-red spectra of these products were compared with those of the saturated products obtained from the reaction of the same hydrocarbons with hydrogen sulphide (Sheppard and Sutherland, this vol., p. 1540). Two general points were noticeable : (*a*) Bands at 890 cm.$^{-1}$ indicated the presence of double bonds of the type $CRR'{:}CH_2$ in the sulphur products. (*b*) There was a strong general resemblance in both cases between the spectra of the products of the reaction with sulphur and those with hydrogen sulphide. In the case of the geraniolene–sulphur product a noticeable splitting of the 1370 cm.$^{-1}$ band indicated a preponderance of *gem*-dimethyl groups (Sheppard and Sutherland, *loc. cit.*), and was further evidence for the similarity of the two products (see below). As the purification of the hydrogen sulphide products led to their identification as 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (I) and 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (II), it seems reasonable to assume that the carbon skeletons of the sulphur products are closely related. On chemical grounds one would expect that the sulphur products would contain a double bond in the molecule, but our spectroscopic data are insufficient to decide this point. However, in view of the fact that the spectra of *cyclo*hexyl and *cyclo*hexenyl groups have many features in common, the spectroscopic data would be consistent with the presence of the above saturated compounds in the products *or*, alternatively, with the presence of similar compounds containing a double bond in the ring. Since $C'RR{:}CH_2$ groups are not obtainable with carbon skeletons of the above type, these bands presumably arise from another molecular species in the product.

(I.)





(II.)

Reductive Scission of Sulphides.—(a) *Action on saturated dialkyl sulphides.* Redistilled di-*n*-butyl sulphide (1 g.; 1 mol.) was dissolved in absolute alcohol (50 c.c.), and sodium (5 g.; 3·2 atoms) added in portions. The alcohol was kept boiling until the sodium had all dissolved, whereupon the product was cooled, poured into water, and the aqueous liquor extracted once with ether to remove traces of unchanged sulphide. The alkaline liquor was then acidified with hydrochloric acid and several times extracted with ether to remove all thiol formed in the reduction. The ethereal extract was freed from traces of mineral acid by washing it with water, and afterwards the content of thiol determined by means of silver nitrate following the procedure of Bell and Agruss (*loc. cit.*). It was found that no appreciable reduction of sulphide to thiol had occurred. The experiment was repeated with pure di-*n*-propyl sulphide, with the same result.

(b) *Action on dialkenyl sulphides.* This was examined with diallyl and di*cyclo*hexenyl sulphides. The amount of hydrogen sulphide and thiol (respectively) produced by reaction were determined from the total yield of –SH groups (including hydrogen sulphide) and the yield of thiol. These values were determined by extracting the hydrogen sulphide and thiol together from one aliquot part of the acidified (H_2SO_4), sulphide-free reduction liquor by means of benzene, and precipitating the hydrogen sulphide from another by means of cadmium chloride, before extracting the thiol from the filtered liquor by means of ether. The details were essentially those of Bell and Agruss (*loc. cit.*). Diallyl sulphide (0·20 g.) became completely reduced, giving approximately equimolecular amounts of hydrogen sulphide (0·0260 g.) and thiol (0·062 g., calc. as allylthiol). Di*cyclo*hexenyl sulphide (0·33 g.) was similarly completely reduced, giving hydrogen sulphide (0·024 g.) and thiol (0·13 g., calc. as *cyclo*hexenthiol).

(c) *Action on alkyl alkenyl sulphides.* These sulphides gave no hydrogen sulphide on reduction, which was incomplete. *cyclo*Hexyl *cyclo*hexenyl sulphide (0·26 g.) gave thiol (doubtless *cyclo*hexyl, 0·091 g.; corresponding to *ca.* 60% reduction); propyl allyl sulphide (0·105 g.) gave thiol (doubtless propyl, 0·033 g., corresponding to *ca.* 50% reduction).

(d) *Action on cyclic sulphides.* The cyclic sulphides from dihydromyrcene and geraniolene were separately reduced in the usual way. Reduction proved to be very incomplete in each case; no hydrogen sulphide was produced but a moderate yield of alkali-soluble thiol was formed from each sulphide.

(e) *Action on thioepoxides.* This was examined only in the instance of *cyclo*hexene thioepoxide. The latter (0·148 g.) gave both hydrogen sulphide (0·010 g.) and thiol (doubtless *cyclo*hexyl, 0·08 g.).

Action of methyl iodide on monosulphides. The sulphide was in each case mixed with an equal volume of the reagent and kept in the dark overnight. A typical saturated sulphide, di*cyclo*hexyl sulphide, gave in good yield the corresponding sulphonium iodide, $SMe(C_6H_{11})_2I$, m. p. 111°. Three dialkenyl sulphides, *viz.*, diallyl, dicrotyl, and 3 : 3′-di*cyclo*hexenyl sulphide, all readily gave crystals of trimethylsulphonium iodide, m. p. 204—207° (decomp.), identical with the compound prepared by union of methyl iodide and methyl sulphide, but no stable sulphonium compound. Two alkyl alkenyl sulphides, *viz.*, *cyclo*hexyl *cyclo*hexenyl sulphide and propyl allyl sulphide, both gave non-crystallising oily products.

The monosulphide from the *cyclo*hexene–sulphur reaction gave much oily material, like the alkyl sulphides, but also a little di*cyclo*hexylmethylsulphonium iodide, m. p. 110° (mixed with authentic specimen, 110°). The cyclic sulphide from dihydromyrcene gave with methyl iodide an oil which slowly crystallised: the resulting solid (colourless prisms, m. p. 130°, from ether–alcohol) was a *methiodide* of dihydromyrcene monosulphide (Found: C, 42·0; H, 7·0; I, 40·5. $C_{11}H_{21}SI$ requires C, 42·3; H, 6·8; I, 40·65%). The cyclic sulphide from geraniolene likewise gave with methyl iodide an oil that slowly crystallised: the solid (colourless prisms, m. p. 120°, from ether–alcohol) was a *methiodide* of geraniolene monosulphide (Found: C, 39·9; H, 6·85; I, 42·25; S, 10·45. $C_{10}H_{19}SI$ requires C, 40·25; H, 6·45; I, 42·55; S, 10·75%).

*cyclo*Hexene episulphide gave with methyl iodide in a few hours much trimethylsulphonium iodide, m. p. 204—207 (Found: C, 17·55; H, 4·45. Calc. for C_3H_9SI: C, 17·7; H, 4·45%).

Removal of Polysulphide Sulphur by Chemical Reagents.—(a) *With sodium hydroxide.* The sample of sulphide was placed in a small flask (*ca.* 10 c.c.) together with 10% or 40% alkali (6 c.c.) and a few c.c. of 0·1% sodium stearate to act as wetting agent. The air space was filled with nitrogen, and the closed vessel mechanically shaken in an oil-bath adjusted to the desired temperature. After the period of treatment was completed the reaction liquor was poured into water, the oily sulphide extracted with benzene, the benzene solution washed well with water and dried (K_2CO_3), and the dry solution filtered and freed from solvent in a vacuum without heating. The decrease in sulphur content due to the action of the alkali was determined by analysis of the specimen before and after treatment in preference to determining the amount of sulphide formed in the reaction.

Typical examples of the effect of the alkali in removing sulphur are the following: The tetrasulphide from *cyclo*hexene decreased in sulphur content from 43·15 to 41·0% in 3 hrs. at 60° with 10% alkali, and from 43·15 to 40·15% in 3 hours at 80° with 40% alkali. The tetrasulphide from *cyclo*hexene decreased in sulphur content from 36·4 to 33·65% in 3 hrs. at 80° with 40% alkali. Diethyl tetrasulphide (from sodium tetrasulphide and ethyl iodide) decreased in sulphur content from 67·4 to 51·5% in 3 hrs. at 80° with sodium hydroxide, so giving nearly pure diethyl disulphide (S, 52·5%).

(b) *With sodium sulphite.* The weighed sample of sulphide (usually *ca.* 0·1 g.) was placed in 10% "AnalaR" sodium sulphite solution (100 c.c.) together with 0·1% sodium stearate (*ca.* 5 c.c.) to act as wetting agent. The solution was boiled for 2·5 hrs. during which nitrogen was slowly bubbled through. Organic matter was extracted with chloroform; then the aqueous phase was cooled at 0°, and 40% formaldehyde solution added to combine with the excess of sodium sulphite. Glacial acetic acid (10 c.c.) and 1% starch solution (3 c.c.) were next added, and the solution titrated with N/10-iodine solution to determine the yield of sodium thiosulphate and hence the amount of sulphur removed (1 mol. of $Na_2S_2O_3 \equiv 1$ atom of S). The following are typical results, losses being given in terms of total sulphur: Ethyl tetrasulphide (from sodium tetrasulphide and ethyl iodide) lost 47·5% (*i.e.*, 1·9 atoms). The polysulphide mixture (excluding cyclic monosulphide) obtained in the geraniolene–sulphur reaction lost 10·8%. The corresponding polysulphide mixture from dihydromyrcene lost 6·4%. Dibutyl tetrasulphide lost 30·1%, and *cyclo*hexene episulphide 45%.

Thermal Decomposition of Polysulphides.—Attempted distillation at *ca.* 0·1 mm. of the sulphurated products from *cyclo*hexene and 1-methyl*cyclo*hexene gave but little distillate (a little monosulphide and no thiol or hydrogen sulphide) unless the temperature of the heating bath was allowed to rise well above 140°. Prolonged heating at higher temperatures caused a slow but progressive distillation of monosulphide, thiol, and hydrogen sulphide. The tendency to decomposition of the monosulphide-free sulphurated product from *cyclo*hexene was examined at 160—170° by heating it in sealed tubes for 5 hours. The tubes were cooled in liquid air before being opened, and the main bulk of hydrogen sulphide present was allowed to evaporate slowly into lead acetate solution. The lead sulphide was filtered off, dried, and weighed. The thiol and residual hydrogen sulphide were estimated by utilising the method of Bell and Agruss (*loc. cit.*). In a typical experiment 13 g. of the sulphuration product yielded hydrogen sulphide (3·8 g.), thiol (2·5 g.), volatile sulphides (mainly monosulphide, 3·3 g.), and a small amount of non-volatile solid which was easily soluble in benzene (3·2 g.). In another experiment 5·9 g. of thio-product, after being kept at 130° and 10^{-5} mm. for 30 hrs. to ensure that no free thiol or lower sulphides were present, gave, on being heated in a sealed tube at 180—190° for 5 hrs., hydrogen sulphide (1·7 g.), thiol (1·2 g.), sulphides (mainly mono-, 1·4 g.), and a dark residue of solid (mainly crystalline) thiohydrocarbon (1·4 g.). The residue, like all residues similarly obtained by the thermal decomposition of sulphurated *cyclo*hexene, had a much reduced H : C ratio (Found : C, 56·35; H, 3·75; S, 39·7%; H : C = 4·75/6).

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WELWYN GARDEN CITY, HERTS.

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