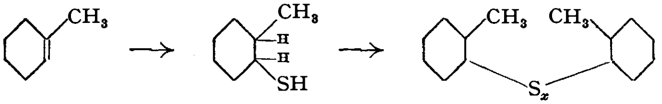
299. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part II. Mechanism of the Reaction of Hydrogen Sulphide with Mono-olefins, Di-isoprenes, and Rubber.*

By Ralph F. Naylor.

Hydrogen sulphide unites with mono- and di-olefins under pressure to give *normal* adducts when reaction is conducted in the presence of sulphur or a metallic sulphide as catalyst, and *abnormal* adducts when it is promoted under the influence of ultra-violet light. The adducts of both types include alkanethiols and alkyl sulphides and disulphides. The principal reaction products from the two di-isoprenes, dihydromyrcene and geraniolene, are cyclic sulphides of the tetrahydrothiopyran series, each being derived from a single molecule of the diolefin; corresponding products derived from two molecules of the diolefin are formed in much smaller yield. Rubber also gives sulphides of the latter (cross-linked) kind, formed by the linking of two or more polyolefin molecules by sulphur.

Apart from the intrinsic interest of the reactivity of hydrogen sulphide with olefins, a knowledge of this reactivity is, as indicated in Part I (preceding paper), of considerable importance in the study of the reaction of sulphur with unsaturated compounds. In marked contrast to the wealth of literature on the addition of hydrogen bromide to olefins, there is very little work recorded on the corresponding reactions of hydrogen sulphide. Such accounts as are published indicate that the addition of hydrogen sulphide is difficult to effect, and that catalysts are invariably required. Among the various catalysts found to be effective are silica gel (Mailhe and Renaudie, *Compt. rend.*, 1932, **195**, 391), nickel on kieselguhr, and certain nickel salts (Duffey, Snow, and Keyes, *Ind. Eng. Chem.*, 1934, **26**, 91; Barr and Keyes, *ibid.*, p. 1111), iron oxide and sulphide (Boëseken and Van der Linde, *Rec. Trav. chim.*, 1935, **54**, 739), and sulphur (Jones and Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2452). The yields of addition products have seldom been high, and the direction of addition has been found in each case to follow the Markownikow rule, although a proportion of *abnormal* addition products was obtained in high-temperature heterogeneous reactions (Barr and Keyes, *loc. cit.*); this probably arose by partial isomerisation of the initial adduct. Recently, however, Vaughan and Rust (*J. Org. Chem.*, 1942, **7**, 472), by ultra-violet irradiation of mixtures of olefins and liquid hydrogen sulphide, have obtained *abnormal* adducts in a short reaction time, without the aid of the high temperatures and pressures found necessary for *normal* addition.

Since it was observed by Jones and Reid (*loc. cit.*) that the normal addition of hydrogen sulphide proceeds far less readily with *cyclo*hexene than with simple aliphatic olefins, it was not surprising to find that photo-addition of liquid hydrogen sulphide to 1-methyl*cyclo*hexene gave poor yields. As Pyrex glass, which was used for the reaction tubes, does not transmit light below 2900 A., whereas hydrogen sulphide is split into radicals only by wave-lengths of 2800 A. or less, it was necessary to add acetone as a photo-sensitiser. The products were a thiol and sulphide, and by analogy with the work of Vaughan and Rust, it may be assumed that these were 1-*methyl*cyclo*hexane-2-thiol* (I), and *di-2-methyl*cyclo*hexyl sulphide* (II). In one experiment the sulphide fraction was found to contain some disulphide (III), which although present in insufficient quantity for separation, was indicated to be present by analytical evidence. Although no previous reference has been made to the formation of disulphides in such reactions, it seems evident that it has arisen either by combination of two mercapto-radicals or by oxidation of the initially formed thiol.



(I.) (II, x = 1; III, x = 2.)

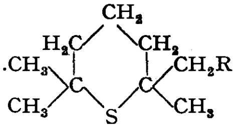
The only recorded work on the catalysis of hydrogen sulphide addition by sulphur (Jones and Reid, *loc. cit.*) suggests that the latter is one of the best catalysts for normal addition, but the relatively large quantities of catalyst then used introduce doubt as to how far the sulphur is itself reacting with the olefins and how far catalysing the addition of hydrogen sulphide. In addition, this work was conducted at 180°, at which temperature there is appreciable decomposition of some di- and poly-sulphides (see Part I; also Hinsberg, *Ber.*, 1910, **43**, 1874). It has now been confirmed that small quantities of sulphur catalyse the addition of hydrogen sulphide to *iso*butylene at *ca.* 140°; some reaction took place in absence of sulphur, but this was probably due to the catalytic effect of ferrous sulphide formed on the walls of the steel autoclave used. The reaction products were identified as being *tert.*-butyl derivatives formed by "normal" addition of the reagent to the double bond, and included di-*tert.*-butyl disulphide as well as the corresponding monosulphide and thiol. The yield of disulphide was greater than could have arisen by reaction of the sulphur catalyst with *iso*butylene, and it was still formed when the catalyst was omitted. The possibility of oxidation of the initially formed thiol was investigated by heating *tert.*-butanethiol with air in a sealed tube; no disulphide could be detected although there was some decomposition of the thiol into *tert.*-dibutyl sulphide and hydrogen sulphide. Rigorous exclusion of air from the *iso*butylene–hydrogen sulphide reaction mixture did not prevent formation of the disulphide, so the only possible mode of reaction seems to be oxidation of the thiol with concurrent reduction (hydrogenation) of the olefin, as reported by Williams and Allen (U.S.P. 2,052,268; *Chem. Abs.*, 1936, **30**, 7122) for similar hydrogen sulphide additions.

*cyclo*Hexene reacted with hydrogen sulphide in presence of a sulphur catalyst in a manner analogous to *iso*butylene, although the *cyclo*hexanethiol first produced appeared to add more readily than hydrogen sulphide to the olefin, since di*cyclo*hexyl sulphide constituted the main product. An attempt to catalyse the addition of hydrogen sulphide to 1-methyl*cyclo*hexene by ethyl dihydrogen phosphate, after the suggestion of Bähr and Corr (D.R.-P. 708,261), was unsuccessful

Sulphur-catalysed addition of hydrogen sulphide to polyisoprenes occurred more readily than it did to hydroaromatic hydrocarbons. Dihydromyrcene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe$, reacted to give a quantity of alkali-soluble material which was too small to permit of isolation of this thiol, but gave a 20% yield of an alkali-insoluble compound of formula $C_{10}H_{20}S$. Of the possible structural formulæ, (IV), (V), and (VI), assignable to this product, (VI), which is formed from (IV) or (V) by an intramolecular addition reaction, seemed the most likely in view of the insolubility of the product in alkali. Inter-molecular addition reaction yielding products containing more than one C_{10}-unit occurred to the extent of only 1—2%, but there appeared to be some unimolecular disulphide ($C_{10}H_{20}S_2$), which was present in insufficient quantity for isolation. Similar results were obtained by interaction of geraniolene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$, with hydrogen sulphide, the main product in this case being a thio-compound $C_9H_{18}S$, represented by (VII), VIII), or (IX). Attempts to obtain characteristic metallic salts or metallic-salt addition compounds were unsuccessful. The infra-red absorption spectrum of this thio-compound was radically different from that of the parent geraniolene, suggesting that a complete change of structure, such as is involved in the formation of a tetrahydrothiopyran ring, might have occurred. An attempt to establish this ring structure by correlation of the spectrum with that of pentamethylene sulphide was unsuccessful, as the latter exhibited an altogether different spectrum from that of the hydrogen sulphide reaction products. Synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (see this vol., p. 1106), although analytically identical with the hydrogen sulphide reaction product, showed differences in boiling point and refractive index, and had a characteristic infra-red absorption spectrum,* which could not be correlated with that of the reaction products. In particular, the latter exhibited absorption associated with unsaturated groupings of the types $CMeR{:}CH_2$ and $CRR'{:}CHR''$ and with thiol groups.

$CMe_2(SH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHR$
(IV, R = CH_3; VII, R = H.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(SH){\cdot}CH_2R$
(V, R = CH_3; VIII, R = H.)



(VI, R = CH_3; IX, R = H.)

---

* Examination of the infra-red absorption spectra of the compounds described in this paper was carried out at Cambridge by Dr. G. B. B. M. Sutherland and Mr. N. Sheppard. The details of the spectra are discussed by these authors in the following paper.

Similar results were obtained with the dihydromyrcene–hydrogen sulphide product. The possibility of the unsaturation being due to the presence of small amounts of unchanged olefin was excluded by two experiments. Dihydromyrcene is a mixture of 2 : 6-dimethylocta-2 : 6-diene, 2 : 6-dimethylocta-2 : 6(10)-diene, and possibly 2 : 6-dimethylocta-1 : 6-diene and therefore shows absorption characteristic of $CMeR{:}CH_2$ grouping. The pure 2 : 6-isomer (which exhibits no such absorption) was prepared by sodium–ammonia reduction of geraniol (Chablay, *Ann. Chim.*, 1917, **8**, 145; Dupont, Dulou, and Desreux, *Bull. Soc. chim.*, 1939, **6**, 84) and reacted with hydrogen sulphide in the presence of sulphur. The resulting product also showed bands characteristic of $CMeR{:}CH_2$ groups, although it was established that no isomerisation of the recovered hydrocarbon had occurred. Also, examination of suitable mixtures showed that introduction of small amounts of dihydromyrcene to the synthetic thiopyran (IX) did not affect the absorption spectrum.

Substitution of aluminium sulphide for sulphur as a catalyst in the reaction of 2 : 6-dimethylocta-2 : 6-diene with hydrogen sulphide gave rise to products similar to the foregoing, but there was isolated in addition, 2 : 6-*dimercapto*-2 : 6-*dimethyloctane*, $CMe_2(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot SH$ (X). The main product, $C_{10}H_{20}S$, showed considerable difference in the absorption attributable to unsaturation from that described above, the predominant group now being $CRR'{:}CHR''$ with very little $CMeR{:}CH_2$. It is evident, therefore, that the $\cdot CMe{:}CH_2$ group arises by reaction of the sulphur itself and not of the hydrogen sulphide. That cyclic sulphides containing this group are in fact among the products of reaction of sulphur with dihydromyrcene has been indicated in Part I (*loc. cit.*).

The improbability of the occurrence in significant degree of a radical mechanism leading to " abnormal " addition in the sulphur-catalysed or metal sulphide-catalysed hydrogen sulphide reaction was indicated by demonstrating that the type of reaction obtained with 2 : 6-dimethylocta-2 : 6-diene was unaffected by the presence of quinol (polyisoprenes usually contain small quantities of peroxide which might catalyse the abnormal addition). However, the ratio of thiol to cyclic sulphides was increased.

In spite of the alkali-insolubility of the compounds $C_{10}H_{20}S$ and $C_9H_{18}S$, Zerewitinoff determinations by the micro-method of Bolland (*Trans. Inst. Rubber Ind.*, 1941, **16**, 267) indicated the presence of varying amounts of active hydrogen, presumably in the form of thiol groups * as had already been indicated by the infra-red spectra. The susceptibility of this method to traces of compounds of low molecular weight containing active hydrogen rendered it less reliable than the method recently described by Turk and Reid (*Ind. Eng. Chem. Anal.*, 1945, **17**, 713) involving titration of a solution of the thiol against a solution of cupric butyl phthalate. The presence of the thiols (IV) and (V), and (VII) and (VIII), in amounts up to 40% of the total $C_{10}H_{20}S$ and $C_9H_{18}S$ fractions was thus demonstrated. A modification of the analytical method allowed cupric butyl phthalate to be used for the qualitative removal of the thiol from the mixtures obtained by the aluminium sulphide-catalysed reactions, and this resulted in the isolation in a nearly pure state of 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (VI) and 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (IX) (see this vol., p. 1106). These two compounds exhibited absorption spectra similar to each other in the infra-red, and in both, all bands associated with unsaturation and thiol groups had disappeared. The geraniolene–hydrogen sulphide product (IX) corresponded in boiling point with the synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran and exhibited similar absorption [notably that associated with the $>CMe_2$ group which is masked in (VI) by single methyl groups] with the addition of some other absorption bands. These extra bands are almost certainly due to reaction products of small amounts of isomers of geraniolene, for, since the preparation of this involves decarboxylation of geranic acid at 270°, a partial isomerisation of the olefin is very probable. This view is confirmed by the nitrous acid test for thiols (Rheinboldt, *Ber.*, 1926, **59**, 1311; 1927, **60**, 184), which indicates that while all the dihydromyrcene products contain only tertiary thiols, those from geraniolene contain at least some primary or secondary thiols. Complete agreement was obtained between the infra-red spectrum of the cyclic sulphide from the reaction of 2 : 6-dimethylocta-2 : 6-diene and hydrogen sulphide and that of synthetic 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (see this vol., p. 1106).

The abnormal addition of hydrogen sulphide to 2 : 6-dimethylocta-2 : 6-diene has been effected by U.V. irradiation of the reactants in the liquid phase, acetone being used as a photo-sensitiser. As in other additions, the main product was a liquid of formula $C_{10}H_{20}S$, which was shown to consist of an approximately 1 : 1 mixture of the monothiols (XI, XII) and

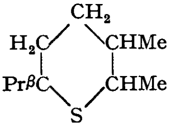
---

* It is known from earlier work that the acidity of thiols decreases progressively with increasing molecular weight (Birch and Norris, *J.*, 1925, **127**, 901).

2 : 3-*dimethyl*-6-iso*propyltetrahydrothiopyran* (XIII). Removal of the thiol by cupric butyl phthalate led to the isolation of a small quantity of the thiopyran (XIII), the absorption spectrum of which exhibited a number of differences from those of the earlier products. In particular, there was some characteristic absorption which was absent in the *normal* adduct (VI), and *vice versa*. Similar differences in the absorption spectrum were exhibited by 3 : 7-*dimercapto*-2 : 6-*dimethyloctane*, $CHMe_2{\cdot}CH(SH){\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CHMe{\cdot}SH$ (XIV), which was also isolated in small yield from the reaction product.

$CHMe_2{\cdot}CH(SH){\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe$
(XI.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CHMe{\cdot}SH$
(XII.)



(XIII.)

In addition, an intermolecularly derived *sulphide*, $C_{20}H_{40}S_2$, formed by union of two monomercapto-units, was isolated; its analytical figures and ·SH content showed it to be a compound of the type (XV), the points of addition of the SH group, on the one hand, and of the union through the S atom, on the other, allowing of three possible isomers (see p. 1539). This is confirmed by its infra-red absorption spectrum, which includes the characteristic absorptions of ·SH and CRR′:CHR″ groups.

$$CHMe_2{\cdot}CH(SH){\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CHMe{\cdot}S{\cdot}CHPr^{\beta}{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe \quad \text{(XV.)}$$

Yields of the various derivatives with the olefins mentioned are indicated in Table I.

TABLE I.

Addition of hydrogen sulphide to olefins.

Olefin.	Molecular proportions (olefin = 1) : H_2S.	Catalyst.	Reaction conditions : hrs.	temp.	Pressure, atm., of H_2S at working temp.	Yields of products, %. Alkali-sol. thiol.	Sulphide.	Disulphide.	Undistillable intermolecular sulphides.
*iso*Butylene	1	0·015 (S)	14	150°	45	7[1]	4	3	0·5
,,	1	—	18	130—150	45	2[1]	—	0·5	Negligible
,,	1	—	14	140	45	2[1]	0·5	0·5	,,
*cyclo*Hexene	2·5	0·015 (S)	24	150	110	2·5	12	1·5	1
						Dithiol.	$C_{10}H_{20}S$ or $C_9H_{18}S$ fraction.	Disulphide.	Intermolecular sulphides.
Dihydromyrcene	2	0·03 (S)	20	130	45	Negligible	13	2	1·5
,,	2	0·03 (S)	22	160	45	,,	18	3	2
Geraniolene	2	0·03 (S)	24	150	50	,,	14	1	1·5
,,	2	0·1 (Al_2S_3) (+ quinol)	26	150	45	[2]	10	0·1	1
2 : 6-Dimethylocta-2 : 6-diene	2	0·03 (S)	22	140—150	45	Negligible	8	[2]	[2]
,,	2	0·1 (Al_2S_3)	23	150—165	60	0·5	10	0·5	0·5
,,	2	0·1 (Al_2S_3) (+quinol)	24	150	50	[2]	8	[2]	[2]
,,	1·2	0·15 ($COMe_2$)	4 (U.V. irradiation)	15	15	2	22	—	5

[1] These figures are too low as some thiol was lost on evaporation of the *iso*butylene.
[2] Not separated.

It was hoped that addition of hydrogen sulphide to rubber might be effected by shaking a rubber solution with the gas while irradiating it with ultra-violet light. However, even after 4 hours' irradiation of a solution of sol rubber (obtained by diffusion of acetone-extracted crepe rubber into light petroleum) only 1·1% of sulphur had entered the molecule. Although quartz apparatus was being used, this figure was doubled when acetone was added as a sensitiser, and small amounts of gelled material separated, which contained up to 10% of sulphur. The best value represents the saturation of 48% of the double bonds of rubber if the sulphur is assumed to be present as monosulphide.

It has been shown by Jones and Reid (*loc. cit.*) that peroxides catalyse the abnormal addition of thiols to olefins. Evidence for the catalytic effect of benzoyl peroxide on the addition of hydrogen sulphide to rubber in the present work was inconclusive. However, it was shown that the addition reaction initiated by ultra-violet light was substantially inhibited by the natural antioxidants in rubber. Quam's report (*J. Amer. Chem. Soc.*, 1925, **47**, 103) that rubber dissolves in liquid hydrogen sulphide was confirmed with milled acetone-extracted crepe, and when the resultant solution was irradiated with ultra-violet light as before, it gave rise to a product containing 2·1% of sulphur. The addition of acetone much reduced the solubility of the rubber, but it increased the sulphur intake to 3·2%.

Solid rubber reacted with hydrogen sulphide both in the presence and in the absence of sulphur, but the latter reaction was probably catalysed by ferrous sulphide on the walls of the steel autoclave. This view was confirmed by the addition of hydrogen sulphide to rubber in the presence of ferrous sulphide and ferric oxide. Although the results obtained with dihydromyrcene and geraniolene suggest that the main reaction with polyisoprenes is intramolecular, there is always some intermolecular addition, and it may well be that this is facilitated in the case of rubber by the intermolecular entanglements of the long chains. A characteristic of all the products which have been obtained from rubber by hydrogen sulphide addition, even when the combined sulphur value is as low as 1%, is their complete insolubility in all organic solvents once they have been separated from solution. It therefore seems evident that intermolecular sulphide and disulphide links of the type observed with *cyclo*hexene and *iso*butylene are being formed. That there is a tendency for the average molecular weight to rise is shown by the fact that the observed molecular weight of a sample of milled rubber rose from 137,000 to 153,000 on treatment with hydrogen sulphide involving the incorporation of only 1% of sulphur. Rubber samples containing 2—3% of sulphur, which had been formed by reaction of solid rubber with hydrogen sulphide, exhibited many of the characteristics of a sulphur-vulcanised rubber, and although the porosity of the product precluded tensile strength tests, selected portions of the sheet were capable of over 700% elongation with good recovery. An attempt to obtain a smooth sheet for such tests by working at atmospheric pressure was unsuccessful, owing to the slowness of addition. The results obtained on both the *abnormal* and *normal* addition of hydrogen sulphide to rubber are summarised in Table II.

TABLE II.

Addition of hydrogen sulphide to rubber.

			Reaction conditions :					S, %, in product.	
Type of rubber.	Solvent.	Sol. concn., %.	Hrs.	Light.	Temp.	press., atm., of H_2S.	Catalyst or sensitiser.	Fractn. remaining in solution.	Insol. fractn.
			Abnormal addition.						
Sol	Benzene	1	4	u.v.			—	1·1	—
Sol	,,	1	4	,,			5% $COMe_2$	2·25	—
Sol	,,	1	4	,,			5% $COMe_2$	2·65	10·1
Sol	,,	1	4	,,			Bz_2O_2 & 5% $COMe_2$	2·1	—
Crepe	,,	1	4	,,			5% $COMe_2$	0·8	—
Milled acetone-extracted crepe	,,	9	7·5	,,			5% $COMe_2$	1·0	4·5 2·2
,, ,,	,,	1	4	daylight			—	0·15	—
,, ,,	,,	1	1	(at 75°)			Bz_2O_2	0·30	—
,, ,,	Liq. H_2S	1	0·4	u.v.			—	2·07	—
,, ,,	,,	1	0·4	,,			5% $COMe_2$	3·2	1·3
			Normal addition.						
Milled crepe	—	—	2		140°	30	—	—	1·85 2·2
,,	—	—	2		140	30	½% S	—	2·7 2·8
,,	—	—	2		140—160	30	—	—	2·75*
,,	—	—	2		140—160	30	½% S	—	3·25*
Milled acetone-extracted crepe	—	—	2		140—160	30	—	—	3·15*
Milled crepe	—	—	2		260	40	—	—	8·45
,,	—	—	48		140	1	—	—	0·5
,,	—	—	48		140	1	½% S	—	0·8
Milled acetone-extracted crepe	*cyclo*Hexane	8	20		85—103	20	FeS & Fe_2O_3	1·1	4·8

* After acetone extraction of the product.

EXPERIMENTAL.

(Microanalyses were carried out by Dr. W. T. Chambers, Miss H. Rhodes, and Miss E. Farquhar.)

Hydrogen sulphide was prepared and purified by Quam's method (*loc. cit.*).

1-*Methyl*cyclo*hexene and Hydrogen Sulphide.*—1-Methyl*cyclo*hexene (10 g.), liquid hydrogen sulphide (7 g.), and acetone (1 g.) were sealed in a Pyrex tube, and irradiated with ultra-violet light for 60 minutes at 0°. The product was extracted with 10% aqueous sodium hydroxide (50 ml.) and with ether. From the alkaline extract was obtained 1-*methyl*cyclo*hexane-2-thiol* (1 g.), which was distilled at 56°/14 mm.; it was an evil-smelling, colourless liquid, which froze when cooled to 0° (Found: C, 63·8; H, 10·8; S, 23·8. $C_7H_{14}S$ requires C, 64·6; H, 10·8; S, 24·6%). The neutral portion, which was very small, distilled at 106°/0·1 mm., and appeared to consist of a mixture of di-2-methyl*cyclo*hexyl sulphide and disulphide (Found: C, 69·8; H, 10·7; S, 18·5. Calc. for $C_{14}H_{26}S$: C, 74·3; H, 11·5; S, 14·2. Calc. for $C_{14}H_{26}S_2$: C, 65·1; H, 10·1; S, 24·8%).

iso*Butylene and Hydrogen Sulphide* (*Sulphur Catalyst*).—A mixture of *iso*butylene (56 g.), solid hydrogen sulphide (38 g.), and sulphur (0·5 g.) was introduced into a steel autoclave and heated for 14 hours at *ca.* 150°. After evaporation of unchanged hydrocarbon the product (12·2 g.) contained *tert.*-butanethiol (6·0 g.), di-*tert.*-butyl sulphide (2·6 g.), di-*tert.*-butyl disulphide (2·8 g.), and a non-volatile residue (0·5 g.). The thiol was redistilled to give a liquid, b. p. 63°, $n_{\mathrm{D}}^{18^\circ}$ 1·4212, and identified as its mercuric salt, m. p. 159—160° (Found: S, 16·8. Calc. for $C_8H_{18}S_2Hg$: S, 16·9%). After thorough extraction with 10% aqueous alkali, the monosulphide distilled at 51°/16 mm. and had $n_{\mathrm{D}}^{18^\circ}$ 1·4511 (Found: C, 65·5; H, 12·3; S, 21·9. Calc. for $C_8H_{18}S$: C, 65·7; H, 12·3; S, 21·9%). Fractionation of the disulphide gave a liquid, b. p. 79—80°/16 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4928 (Found: C, 53·9; H, 10·2; S, 35·9. Calc. for $C_8H_{18}S_2$: C, 53·9; H, 10·1; S, 35·9%).

In absence of sulphur, 14 hours' heating of a mixture of *iso*butylene (56 g.) and hydrogen sulphide (38 g.) gave a product containing *tert.*-butanethiol (1 g.), di-*tert.*-butyl sulphide (0·6 g.), and di-*tert.*-butyl disulphide (0·7 g.). In a further similar experiment, when air was completely excluded, after 18 hours at 130—150° the product consisted of thiol (1·5 g.), disulphide (0·4 g.), and a negligible quantity of sulphide.

tert.-Butanethiol (2 g.) was heated in a sealed tube in presence of air for 14 hours at 140—150°; it was mainly unchanged but contained di-*tert.*-butyl sulphide (0·2 g.) and hydrogen sulphide.

cyclo*Hexene and Hydrogen Sulphide* (*Sulphur Catalyst*).—A mixture of *cyclo*hexene (100 g.), hydrogen sulphide (100 g.), and sulphur (0·5 g.) was heated for 24 hours at *ca.* 150°. Fractional distillation of the product gave *cyclo*hexanethiol (3·5 g.), di*cyclo*hexyl sulphide (13·5 g.), di*cyclo*hexyl disulphide (2·5 g.), and a residue (1·5 g.). The thiol was purified by conversion with 10% aqueous alkali into its sodium salt, whose solution was acidified with hydrochloric acid under nitrogen; the redistilled thiol had b. p. 41°/12 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4988 (Found: C, 62·1; H, 10·2; S, 27·3. Calc. for $C_6H_{12}S$: C, 62·0; H, 10·3; S, 27·6%). To an alcoholic solution of the thiol was added hot aqueous mercuric cyanide. The precipitated oil was dissolved in hot alcohol and left to crystallise; on recrystallisation from methanol the *mercaptide* was obtained as colourless crystals, m. p. 71° (Found: S, 14·9; Hg, 46·4. $C_{12}H_{22}S_2Hg$ requires S, 14·9; Hg, 46·4%). The redistilled sulphide was a colourless liquid, b. p. 74°/0·2 mm., $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·5162 (Found: C, 72·5; H, 11·1; S, 16·2. Calc. for $C_{12}H_{22}S$: C, 72·7; H, 11·1; S, 16·2%), and the disulphide a pale yellow liquid b. p. 110—112°/0·2 mm., $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·5557 (Found: C, 63·0: H, 9·7; S, 27·4. Calc. for $C_{12}H_{22}S_2$: C, 62·7; H, 9·6; S, 27·8%). On standing with methyl iodide the monosulphide yielded a yellow oil which slowly solidified to the *methiodide* of di*cyclo*hexyl sulphide; recrystallisation from ether containing a little alcohol gave colourless crystals, m. p. 110—111° (Found: I, 37·4. $C_{13}H_{25}SI$ requires I, 37·2%). This m. p. is the same as that obtained by Meyer and Hohenemser for the methiodide derived from the partly unsaturated sulphide (*Helv. Chim. Acta*, 1935, **18**, 1061).

Dihydromyrcene.—Myrcene, prepared from bay oil (*Pimenta acris*) by the method of Power and Kleber (*Pharm. Rundschau*, 1895, **13**, 60), was reduced with sodium and alcohol as described by Semmler and Mayer (*Ber.*, 1911, **44**, 2010). The hydrocarbon, after being twice fractionally distilled over sodium, had b. p. 60°/16 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4542 (Found: C, 87·2; H, 12·9. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%).

Dihydromyrcene and Hydrogen Sulphide (*Sulphur Catalyst*).—A mixture of dihydromyrcene (69 g.), hydrogen sulphide (38 g.), and sulphur (0·5 g.) was heated in the autoclave for 20 hours at *ca.* 130°. On fractionation of the product the b. p. rose steadily from 50 to 90°/9 mm. and then from 68° to 80°/1 mm.; apart from unchanged dihydromyrcene, the distillate contained a mixture of isomeric monothiols, cyclic monosulphide (*ca.* 11 g.), and cyclic disulphide (2 g.), and a polymeric residue (1 g.) remained. The distillate fractions were extracted with 10% aqueous alkali in absence of air, and the extract after acidification was extracted with ether. Only a drop of liquid was thus obtained, but its odour was definitely mercaptan-like. Fractional distillation of the sulphide fractions gave a mixture of the $C_{10}H_{20}S$ isomers, (IV), (V), and (VI), b. p. 83°/9 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4858 (Found: C, 69·9; H, 11·4; S, 18·6. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%). With methyl iodide this product gave an oil, which on long standing yielded yellow crystals of the *methiodide*, m. p. 126—127° (decomp.) in insufficient quantity for complete purification (Found: I, 39·1. $C_{11}H_{23}I$ requires I, 40·3%). No pure *disulphide* was isolable but it was present to large extent in the higher fractions, such as one, b. p. 70°/1 mm., $n_{\mathrm{D}}^{15\cdot5^\circ}$ 1·5202 (Found: C, 60·7; H, 10·0; S, 28·6. $C_{10}H_{20}S_2$ requires C, 58·8; H, 9·8; S, 31·3%).

A similar reaction between dihydromyrcene and hydrogen sulphide in the presence of sulphur, conducted at 160° for 22 hours, gave a product containing the $C_{10}H_{20}S$ isomers (15 g.), disulphide (3 g.), and polymeric compounds (1·5 g.).

The combined hydrocarbon fractions from the above experiments were again extracted with alkali, washed with water, dried (K_2CO_3), and distilled through a Fenske column. The recovered dihydromyrcene had b. p. 60°/16 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4511, and was shown by analytical and absorption-spectra measurements not appreciably to have cyclised or isomerised (Found: C, 87·2; H, 12·9; I.V., **362**. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%; I.V., 368).

Geraniolene.—Citral was oxidised with silver oxide (Bernhauer and Forster, *J. pr. Chem.*, 1936, **147**, 199), and the resulting geranic acid was decarboxylated at 260—270° (Tiemann and Semmler, *Ber.*, 1893, **26**, 2724) to give geraniolene, b. p. 36°/10 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·4408 (Found : C, 87·0; H, 12·9; I.V., 385. Calc. for C_9H_{16} : C, 87·1; H, 12·9%; I.V. 409). The low I.V. indicated the presence of some cyclised isomer.

Geraniolene and Hydrogen Sulphide (*Sulphur Catalyst*).—A mixture of geraniolene (70 g.), hydrogen sulphide (45 g.), and sulphur (0·5 g.) was heated in the autoclave for 24 hours at 150°. Distillation of the product gave a mixture of isomeric monothiols and cyclic monosulphide (12·5 g.), disulphide (1 g.), and a polymeric residue (1·5 g.). From the monosulphide fraction was obtained a pure mixture of the $C_9H_{18}S$ isomers (VII), (VIII), and (IX), b. p. 87°/16 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·4812 (Found : C, 68·2; H, 11·4; S, 20·2. Calc. for $C_9H_{18}S$: C, 68·4; H, 11·4; S, 20·2%). Reaction of this product with methyl iodide at 15° gave an oil which would not solidify. The fraction containing the highest percentage of *disulphide* had b. p. 75°/1 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·5100 (Found : C, 59·0; H, 10·1; S, 29·3. $C_9H_{18}S_2$ requires C, 56·9; H, 9·5; S, 33·7%).

Geraniolene and Hydrogen Sulphide (*Aluminium Sulphide Catalyst*).—A mixture of geraniolene (42 g.), recovered from the foregoing experiment), hydrogen sulphide (38 g.), aluminium sulphide (6 g.), and quinol (2 g.) was heated in the autoclave in the absence of air for 26 hours at *ca.* 150°. The product in ethereal solution was thoroughly extracted with 10% aqueous sodium hydroxide, washed with water, and dried (Na_2SO_4). On exposure to air the alkaline extract immediately started oxidising, with the formation of a viscous red oil (evidently a polymeric disulphide). Fractional distillation of the ethereal extract gave the $C_9H_{18}S$ isomeric mixture (5·2 g.), with b. p. ranging from 69—71°/11 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·4729 (Found : C, 68·5; H, 11·2; S, 19·9; ·SH, 8·7%), to 80—81°/11 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·4778 (Found : C, 67·9; H, 11·4; S, 20·3; ·SH, 12·3. Calc. for $C_9H_{18}S$: C, 68·4; H, 11·4; S, 20·2; ·SH, 0%. Calc. for $C_9H_{17}{\cdot}SH$: ·SH, 20·9%). No disulphide was isolable, although one fraction (1·0 g.) contained a small proportion thereof (Found : S, 22·1. Calc. for $C_9H_{18}S$: S, 20·2. Calc. for $C_9H_{18}S_2$: S, 33·6%). An intermolecular sulphide fraction (0·5 g.), b. p. 117—122°/0·5 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·4988, was isolated, and it appeared to be mainly the compound $C_9H_{17}S{\cdot}C_9H_{18}{\cdot}SH$ (see p. 1539) containing some $C_9H_{17}{\cdot}S{\cdot}C_9H_{17}$ (Found : C, 70·0; H, 11·1; S, 18·7. Calc. for $C_{18}H_{36}S_2$: C, 68·4; H, 11·4; S, 20·2%. Calc. for $C_{18}H_{34}S$: C, 76·6; H, 12·0; S, 11·3%).

Separation of the $C_9H_{18}S$ *isomers.* An approximately 0·2N-solution of cupric butyl phthalate (Turk and Reid, *loc. cit.*) was prepared by dissolving the reagent (5·1 g.) in 100 ml. of *n*-propyl alcohol containing acetic acid (5 ml.). This reagent was introduced into a solution of the $C_9H_{18}S$ mixture (3·3 g.) in *n*-propyl alcohol (50 ml.) until the green colour just persisted. After dilution with water to 800 ml. the product was extracted with chloroform, washed with water, dried, and fractionally distilled. After refractionation, 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (IX) (1 g.) was obtained as a colourless liquid, b. p. 64—66°/11 mm., $n_{\mathrm{D}}^{18^{\circ}}$ 1·4732 (Found : C, 68·4; H, 11·3; S, 19·9. Calc. for $C_9H_{18}S$: C, 68·4; H, 11·4; S, 20·2%).

Reaction of (IX) with methyl iodide at 0° gave only an oil, but when the sulphide was heated with excess of methyl iodide at 100° for 12 hours, yellow crystals separated, which after being washed with methanol and recrystallised from ethanol decomposed at *ca.* 200° and proved to be trimethylsulphonium iodide (Found : S, 15·7; I, 61·9. Calc. for C_3H_9SI : S, 15·7; I, 62·2%).

2 : 6-*Dimethylocta*-2 : 6-*diene*.—Geraniol was purified by conversion into its calcium chloride compound, and then reduced by sodium in liquid ammonia (Chablay; Dupont, Dulou, and Desreux, *locc. cit.*). After fractional distillation over sodium, the pure hydrocarbon had b. p. 56°/14 mm., $n_{\mathrm{D}}^{17^{\circ}}$ 1·4517 (Found : C, 87·0; H, 13·2; I.V., 370. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%; I.V., 368).

2 : 6-*Dimethylocta*-2 : 6-*diene and Hydrogen Sulphide* (*Normal Addition*).—A mixture of the olefin (69 g.), hydrogen sulphide (38 g.), and sulphur (0·5 g.) was heated in absence of oxygen under pressure for 22 hours at 140—150°. After extraction with aqueous alkali, fractional distillation of the product gave a mixture of $C_{10}H_{20}S$ isomers (5 g.) and a higher-boiling fraction which in this instance was not separated. Refractionation of the former yielded the $C_{10}H_{20}S$ isomers, b. p. 92—94°/18 mm., $n_{\mathrm{D}}^{20^{\circ}}$ 1·4842 (Found : C, 69·8; H, 11·5; S, 18·3. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%); this fraction contained about 11% of the monothiol (Found : ·SH, 2·1. Calc. for $C_{10}H_{19}SH$: ·SH, 19·2%). The unreacted olefin was recovered and shown to be uncyclised 2 : 6-dimethylocta-2 : 6-diene, b. p. 54°/13 mm., $n_{\mathrm{D}}^{17^{\circ}}$ 1·4501 (Found : C, 87·0; H, 13·2; I.V., 370. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%; I.V., 368).

In a further similar experiment 2 : 6-dimethylocta-2 : 6-diene (92 g.) was treated with hydrogen sulphide (58 g.) in the presence of aluminium sulphide (10 g.) for 23 hours at 150—165°. After extraction with 10% aqueous sodium hydroxide solution, the product was distilled as before to give the $C_{10}H_{20}S$ fraction (11 g., b. p. *ca.* 76—89°/9 mm.), disulphide (0·5 g., not isolable), and a residue of intermolecular sulphides (0·5 g.). On refractionation of the $C_{10}H_{20}S$ fraction, a product was obtained, b. p. 87—88°, $n_{\mathrm{D}}^{16^{\circ}}$ 1·4798 (Found : C, 69·6; H, 11·6; S, 18·6. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%), which contained *ca.* 27% of the monothiol 2(or 6)-mercapto-2 : 6-dimethyloct-6(or 2)-ene (Found : ·SH, 5·1. Calc. for $C_{10}H_{19}{\cdot}SH$: ·SH, 19·2%). Treatment of this product with copper butyl phthalate, in a manner analogous to that used for separation of the $C_9H_{18}S$ isomers, led to the isolation of 2 : 2 : 6-trimethyl-6-ethyl-tetrahydrothiopyran, b. p. 84°/10 mm., n_{D}^{20} 1·4792 (Found : C, 69·4; H, 11·5, S, 18·3. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%). Reaction with methyl iodide at 0—15° gave an oil which crystallised only extremely slowly, and reaction at 100° gave trimethylsulphonium iodide (Found : S, 15·7; I, 61·9. Calc. for C_3H_9SI : S, 15·7; I, 62·2%). By acidification of the alkali extract and subsequent extraction with ether was obtained 2 : 6-*dimercapto*-2 : 6-*dimethyloctane* (0·5 g.), b. p. 110°/9 mm., $n_{\mathrm{D}}^{16^{\circ}}$ 1·4971 (Found : C, 58·2; H, 10·6; S, 31·0; ·SH, 32·0. $C_{10}H_{22}S_2$ requires C, 58·3; H, 10·7; S, 31·0; ·SH, 32·0%).

In a third experiment a mixture of 2 : 6-dimethylocta-2 : 6-diene (77 g.), hydrogen sulphide (48 g.), aluminium sulphide (8 g.), and quinol (2 g.) was heated for 24 hours at *ca.* 150°. From the $C_{10}H_{20}S$ fraction (7·5 g.) was obtained a mixture of isomers, b. p. 86—8°/10 mm., $n_{\mathrm{D}}^{20^{\circ}}$ 1·4782 (Found : C, 69·7; H, 11·5; S, 18·7. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%), which contained 42% of the monothiol (Found : ·SH, 8·0. Calc. for $C_{10}H_{19}SH$: ·SH, 19·2%). Removal of the latter by the copper butyl phthalate method left somewhat impure 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran, b. p. 80—83°/11 mm., $n_{\mathrm{D}}^{14^{\circ}}$ 1·4806 (Found : C, 70·7; H, 11·6; S, 17·5. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%).

2 : 6-*Dimethylocta*-2 : 6-*diene and Hydrogen Sulphide* (*Abnormal Addition*).—Two Pyrex tubes, each containing the olefin (18·3 g.), hydrogen sulphide (5·1 g.), and acetone (1·2 g.), were sealed under vacuum and irradiated with U.V. light at 15° for 4 hours. After extraction with 10% aqueous alkali, the product was fractionally distilled to give a $C_{10}H_{20}S$ isomeric mixture (9 g.) and intermolecular sulphides (2 g.). From the former was obtained a fraction, b. p. 92—92·5°/11 mm., $n_D^{19.5°}$ 1·4767 (Found : C, 69·8; H, 11·6; S, 18·6. Calc. for $C_{10}H_{20}S$ requires C, 69·8; H, 11·6; S, 18·6%), which contained 56% of the monothiol, 3(or 7)-mercapto-2 : 6-dimethyloct-6(or 3)-ene (Found : ·SH, 10·8. $C_{10}H_{19}$·SH requires ·SH, 19·2%). Removal of the thiol by the copper butyl phthalate method left 2 : 3-*dimethyl*-6-iso*propyltetrahydrothiopyran*, b. p. 46°/1 mm., $n_D^{15°}$ 1·4831 (Found : C, 69·7; H, 11·5; S, 18·2. $C_{10}H_{20}S$ requires C, 69·8; H, 11·6; S, 18·6%). Acidification of the alkaline extract liberated 3 : 7-*dimercapto*-2 : 6-*dimethyloctane*, b. p. 132°/11 mm., $n_D^{17°}$ 1·5025 (Found : C, 58·3; H, 11·0; S, 30·8. $C_{10}H_{22}S_2$ requires C, 58·3; H, 10·7; S, 31·0%). Fractionation of the intermolecular sulphide fraction led to the separation of 5(or 2)-*mercapto*-1 : 2 : 6-*trimethylheptyl* 4-*methyl*-1-iso*propylhex*-4-*enyl sulphide* or the 1 : 5-*dimethyl*-1-*ethylhex*-4-*enyl sulphide* (as XV), b. p. 147°/0·1 mm., $n_D^{15.5°}$ 1·4990 (Found : C, 69·4; H, 11·6; S, 18·8; ·SH, 10·0. $C_{20}H_{40}S_2$ requires C, 69·8; H, 11·6; S, 18·6; ·SH, 9·6%).

Nitrous Acid Test for Thiols.—Dilute sulphuric acid was slowly added to an alcoholic solution of the thiol containing solid sodium nitrite, through which nitrogen was bubbling (Rheinboldt, *loc. cit.*). All the products of normal addition of hydrogen sulphide to dihydromyrcene and 2 : 6-dimethylocta-2 : 6-diene gave green oils which appeared red in bulk when viewed by transmitted light; this was indicative of the tertiary grouping CRR′R″·SH. The U.V.-light-catalysed reaction product gave a bright red oil indicating the secondary grouping CHRR′·SH (the formation of a primary thiol not being feasible in this reaction), and the geraniolene products a reddish oil, which pointed to the presence of at least some secondary thiol.

Rubber and Hydrogen Sulphide (*Abnormal Addition*).—A 1% benzene solution of sol rubber was shaken with hydrogen sulphide in absence of air, and irradiated in a quartz flask with ultra-violet light for 4 hours. The product after separation by precipitation with alcohol and drying in a high vacuum contained 1·1% of sulphur. The experiment was repeated using as solvent benzene containing 5% of acetone as photosensitiser. From two runs the products contained 2·25 and 2·65% of sulphur severally; a very small quantity of rubber came out of solution as a gel, and in the latter case this contained 10·1% of sulphur. When crepe containing its natural antioxidants was used, the sulphur value obtained was 0·8%. Seven hours' irradiation of a 9% solution of milled acetone-extracted crepe in benzene containing 5% of acetone gave small quantities of gels containing 4·5—2·2% of sulphur, and a main product with 1% (*M*, 153,000). The same conditions, 1% solutions being used without irradiation, led to incorporation of only 0·15% of sulphur. A further solution was saturated with hydrogen sulphide at 0° and then heated with benzoyl peroxide for 1 hour at 75°; this increased the sulphur intake to 0·30%.

Milled acetone-extracted crepe (0·5 g.) and liquid hydrogen sulphide (30 ml.) were sealed in a Pyrex tube. After 3 days with occasional gentle shaking the rubber pased into solution, and was then irradiated for 25 minutes at 15°; the product contained 2·07% of sulphur. On repetition of the experiment with milled crepe (0·7 g.), hydrogen sulphide (24 ml.), and acetone (1·2 ml.), the rubber did not go wholly into solution. The analyses of the two portions after 25 minutes irradiation were : Found, for insoluble fraction, C, 85·6; H, 11·6; S, 1·3; ash, 0·17; 0 (diff.), 1·3%. Found, for soluble fraction, C, 85·0; H, 11·65; S, 3·2; ash, 0·09; 0 (diff.), 0·06%. It is evident that liquid hydrogen sulphide preferentially dissolved the pure hydrocarbon, as the starting material contained 1·0% of oxygen.

Rubber and Hydrogen Sulphide (*Normal Addition*).—Similar 1-mm. sheets (10 g.) of crepe rubber, milled alone and with ½% of sulphur, were heated with hydrogen sulphide (24 g.) in the autoclave in absence of air for 2 hours at 140°. The products, although full of small hydrogen sulphide bubbles, were elastic like sulphur-vulcanised rubber (Found, for uncatalysed product; S, 1·9: 2·2. For catalysed product : S, 2·7, 2·8%). After a similar reaction at 140—160° the products were acetone-extracted to remove free sulphur (Found, for uncatalysed product : S, 2·75. For catalysed product : S, 3·25%); at this temperature acetone-extracted crepe rubber reacted to give a product (Found : S, 3·15%) after further acetone-extraction. Reaction of milled crepe (10 g.) with hydrogen sulphide (24 g.) for 2 hours at 260° yielded a product in which some chain fission had obviously taken place (Found : S, 8·5%). Sheets of milled crepe with and without ½% of sulphur were heated at 140° for 48 hours in hydrogen sulphide at atmospheric pressure (Found, for uncatalysed product: S, 0·5; for catalysed product, S, 0·8%); a control sample heated in nitrogen was unchanged.

An 8% solution (250 ml.) of milled acetone-extracted crepe rubber in *cyclo*hexane, liquid hydrogen sulphide (50 g.), ferrous sulphide (4 g.), and ferric oxide (2 g.) were sealed in the autoclave in absence of air and heated for 20 hours at 85—103°. Some rubber (3—4 g.) came out of solution as a gel (Found : S, 4·8%). The main solution was centrifuged to remove catalyst, and the rubber precipitated by alcohol (Found : S, 1·1%).

This paper forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The author wishes to express his thanks to Dr. E. H. Farmer for his advice and criticism, to Dr. G. B. B. M. Sutherland and Mr. N. Sheppard for examination of the infra-red absorption spectra and for valuable discussions on their inference, and to Dr. G. Gee for the molecular-weight determinations.

British Rubber Producers' Research Association,
48, Tewin Road, Welwyn Garden City, Herts.

[*Received, January* 15*th*, 1947.]