977. *The Synthesis and Characterisation of Isomeric Di(methylpentenyl) Sulphides and Disulphides.*

By M. B. Evans, G. M. C. Higgins, B. Saville, and A. A. Watson.

Identification of the products of accelerated sulphuration of 2-methylpent-2-ene has necessitated the synthesis of a number of isomeric di(methylpentenyl) mono- and di-sulphides, to be used for calibration purposes in the analysis of complex sulphidic mixtures. The synthesis of the required compounds and their characterisation are described.

Trialkylethylenes (RH), sulphur, and zinc oxide, in the presence of vulcanisation accelerators and other additives, react over a wide temperature range to yield principally mixtures of dialkenyl mono-, di-, and poly-sulphides (RS_xR, $x = 1, 2$, and higher) according to the stoicheiometry:

$$2RH + (x + 1)S + ZnO \longrightarrow RS_xR + ZnS + H_2O,$$

where H of RH is α-methylenic or α-methylic to the ethylenic bond.[1,2] Limited knowledge of the constitution of the alkenyl portions (R in RS_xR) has been obtained from ozonolytic [1] and infrared spectroscopic [2] examination. However, a mechanistic understanding of the sulphuration process demands detailed identification of the sulphidic mixture RS_xR, and this in turn requires authentic reference compounds corresponding to individual forms

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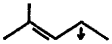
[1] Armstrong, Little, and Doak, *Ind. Eng. Chem.*, 1944, **36**, 628.

[2] Farmer, Ford, and Lyons, *J. Appl. Chem.*, 1954, **4**, 554.

of RS_xR and analytical procedures for their determination in multicomponent mixtures. Preliminary examination by infrared spectroscopy [2] of the sulphidic products of a number of reactions of 2-methylpent-2-ene (I) with sulphur and auxiliary reagents indicated

$$Me_2C = CH \cdot CH_2 \cdot CH_3 \quad (I)$$

that whilst the unsaturation was mainly trialkylethylenic an appreciable proportion of terminally-unsaturated and *trans*-dialkylethylenic groups were also present. It was also known that saturated methylpentyl groups are abundant in the products of unaccelerated sulphuration of 2-methylpent-2-ene.[3,4] This evidence suggested that seven important groups [(II)—(VIII)] might be involved in defining the structures of the products of accelerated sulphuration of 2-methylpent-2-ene.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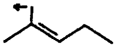
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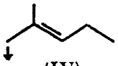
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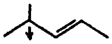
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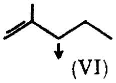
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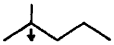
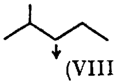
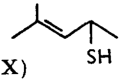
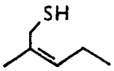

(VII)


(VIII)

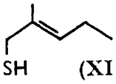
It can then be seen that 28 different sulphides might be required for reference in a comprehensive analysis of the monosulphides from sulphurations of the olefin (I). The same argument also holds for disulphides. We now report on the synthesis and



(IX)

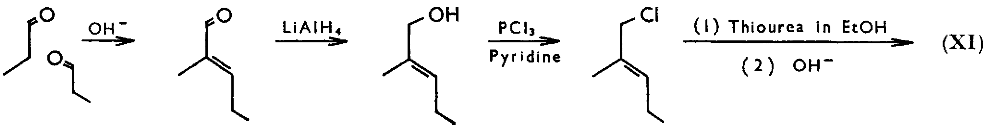


(X)



(XI)

characterisation of the more important of these compounds, and commence by considering compounds containing only trialkylethylenic groups (II—IV). 4-Methylpent-3-ene-2-thiol (IX) has been reported recently.[5] 2-Methylpent-2-ene-1-thiol [*cis* = (X); *trans* = (XI)] was synthesised from propionaldehyde according to the scheme:



(XII) (XIII) (XIV)

Our justification for suggesting that the thiol produced is mainly *trans*-2-methylpent-2-ene-1-thiol (XI) is based on theoretical consideration of the stereochemistry of the elimination of water from the intermediate aldol in the treatment of propionaldehyde with base, so that the unsaturated aldehyde (XII) is *trans* (cf. analogous *trans*-configuration in crotonaldehyde). This configuration should not be altered when the aldehyde is reduced to the alcohol,[6] and since *trans*-crotyl alcohol gives *trans*-crotyl chloride without rearrangement with phosphorus trichloride and pyridine [7] the subsequent stages in the above synthetical route also lead to essentially *trans*-2-methylpent-2-enyl derivatives. The recrystallised thiuronium salt [from (XIV) and thiourea in boiling ethanol] was hydrolysed to the corresponding thiol which was isolated by steam distillation and further fractionation. Gas–liquid chromatographic analysis showed the thiol fractions to be substantially the *trans*-thiol (XI) and to contain two minor components. The concentration of one of these components was seen to be directly proportional, throughout several fractions, to spectroscopic estimates of Δ^1-unsaturation. Accordingly, this minor component is assigned structure (XV), a logical choice also in terms of the mechanism of nucleophilic substitution at 2-methylpent-2-enyl centres. The other minor component,

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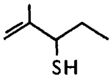
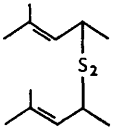
[3] Bateman, Glazebrook, Moore, Porter, Ross, and R. W. Saville, *J.*, 1958, 2838.
[4] Moore and Porter, unpublished.
[5] B. Saville, preceding paper.
[6] Green and Hickinbottom, *J.*, 1957, 3262.
[7] Hatch and Nesbitt, *J. Amer. Chem. Soc.*, 1950, **72**, 727.

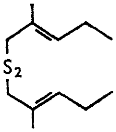
which must be an isomeric thiol, and which was only partly resolved chromatographically from (XI), is almost certainly (X). The best preparations of the thiol contained approximately 95% of (XI), 3% of (X), and 2% of (XV).



(XV)



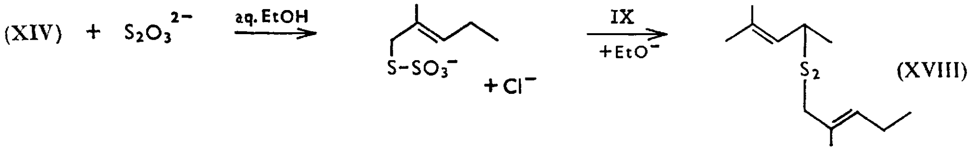
(XVI)



(XVII)

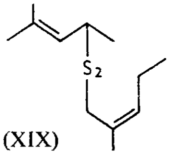
The disulphides (XVI) and (XVII) were obtained on oxidation of the corresponding thiols, (IX) and (X), respectively, with alkaline hydrogen peroxide.[8]

When the disulphide (XVII), written above as the di-(*trans*-2-methylpent-2-enyl) derivative, was reduced with lithium aluminium hydride the recovered thiol was found by gas-liquid chromatographic analysis to be (XI; 70%) and (X; 30%), although the thiol taken for the original oxidation was (XI; 95%). Obviously opportunities exist in the oxidation process for *cis–trans*-interconversions.† The unsymmetrical disulphide (XVIII) was obtained as a 96% pure product by the following route:

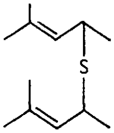


It was necessary to avoid reaction of a two-phase system of the chloro-olefin (XIV), sodium thiosulphate, water, and ethanol to effect the formation of the *S*-alkenylthiosulphate ion in the first step in order to prevent the competing solvolysis of (XIV) which, by yielding acid, leads to extensive decomposition of thiosulphate ion. The formation of the intermediate *S*-alkenylthiosulphate was most conveniently brought about by use of cyclohexylammonium thiosulphate in a single aqueous ethanol phase. Treatment of the *S*-alkenylthiosulphate solution with the thiol (IX) (dissolved in one equivalent of sodium ethoxide in ethanol) gave the required unsymmetrical disulphide (XVIII), which was characterised by reduction with lithium aluminium hydride [9] to equal quantities of (IX) and (X + XI). Thus the disulphide (XVIII) actually contained some of the *cis*-2-methylpent-2-enyl isomer (XIX), although this was not separated chromatographically from (XVIII).

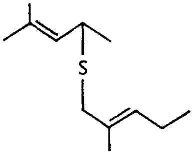
The acid-catalysed addition of thiols to 2-methylpenta-1,3-diene [5] was used to provide the monosulphides (XX) and (XXI). Thus, when the thiol (IX) was added to the diene in the presence of a trace of perchloric acid [5] the resulting dialkenyl sulphide consisted of two main components having closely similar retention times (polyethylene glycol stationary phase) together with a small (*ca.* 5%) constituent later identified as the sulphide (XXII). The latter impurity could be virtually eliminated by careful distillation of the product. It is almost certain that the two main components then remaining are the *meso* and racemic modifications of (XX), evidence for which was obtained from fractional



(XIX)



(XX)



(XXI)

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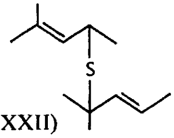
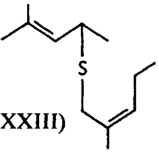
† Subsequent work has shown that this *cis–trans*-interconversion most probably occurs during final distillation of the disulphide (XVII).

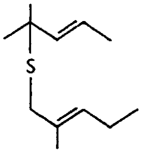
[8] McAllan, Cullum, Dean, and Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3627.

[9] Porter, Saville, and Watson, *J.*, in the press.

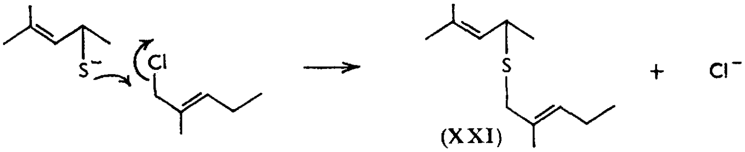
freezing of the sulphide at —80°. This led to samples of the sulphide in which the weight ratio of the two components could be markedly altered without the slightest change in infrared spectra which were consistent only with that of a trialkylethylenic compound.


(XXII)


(XXIII)

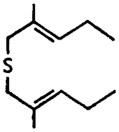

(XXIV)

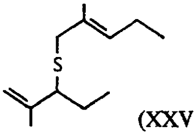
Similar addition of (XI; 95%) to 2-methylpenta-1,3-diene gave the sulphide (XXI) with a little (XXIII) and (XXIV). The sulphide (XXI) was obtained isomerically purer (96%) by reaction of the sodium salt of the thiol (IX) with the chloride (XIV) in ethanol.



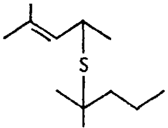
(XXI)

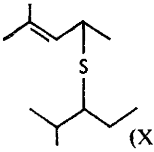
Reaction of the chloro-olefin (XIV) with sodium sulphide (½ equiv.) or with the sodium salt of the thiol (XI) gave 93% of (XXV) (with a little *cis*-material) and 7% of (XXVI), the latter being confirmed by infrared spectral analysis and comparison with authentic sulphide (XXVI) whose synthesis is described below.

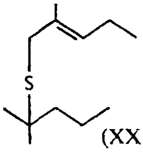

(XXV)

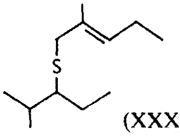

(XXVI)

The alkenyl alkyl monosulphides (XXVII) and (XXVIII) have been described recently,[5] and the corresponding 2-methylpent-2-enyl derivatives (XXIX) and (XXX) were obtained through the action of the sodium salts of 2-methylpentane-2-thiol and 2-methylpentane-3-thiol on the chloro-olefin (XIV) in ethanol.

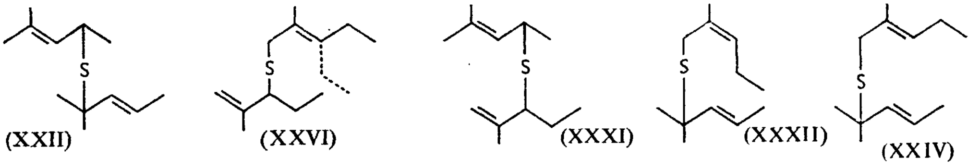

(XXVII)


(XXVIII)


(XXIX)

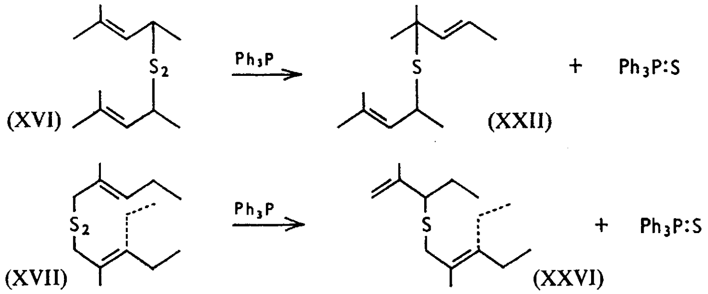

(XXX)

So far we have considered the important structures in which the alkenyl groups are trialkylethylenic. We now describe five sulphides which combine the alkenyl groups (II) and (III) ⟷ (IV) with (V) and (VI) through single sulphur atoms to give the unsymmetrical structures:


(XXII) (XXVI) (XXXI) (XXXII) (XXIV)

(Dotted lines indicate alternative *cis*-structures.)

The isomers (XXII) and (XXVI), already recognised as impurities in earlier preparations of trialkylethylenic sulphides, were readily prepared by the reaction [10,11] of triphenylphosphine with (XVI) and (XVII) respectively in the absence of solvent for 72 hours at 80°. During these reactions an atom of sulphur is removed from the disulphide and one of the alkenyl groups undergoes almost complete allylic rearrangement [10,11] so that the changes (II) ⟷ (V), and (III) or (IV) ⟷ (VI) are observed for the processes:



(XVI) (XXII) (XVII) (XXVI)

Sulphides (XXII) and (XXVI), prepared by the method of Moore and Trego,[11] were characterised mainly through the use of chromatographic and spectral techniques. In each case substantially one-component products were obtained which contained appropriate proportions of the expected unsaturation types.

Methods for preparing substantially pure specimens of (XXIV), (XXXI), and (XXXII) have not been devised, but it was expected that they would be constituent products of the reaction:

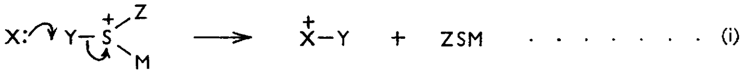
$$[\text{(XVIII) and (XIX)}] + Ph_3P \longrightarrow [\text{(XXIV), (XXXI), and (XXXII)}] + Ph_3P{:}S$$

Use of mutually reinforcing analytical techniques then led to the assignment of appropriate structures to the products of the reaction and yielded gas–liquid chromatographic retention data for (XXIV), (XXXI), and (XXXII). Of particular value in reaching these assignments was a novel chemical analysis the basis of which is now considered.

Silver Ion-assisted Solvolysis of Isomeric Di(methylpentenyl) Sulphides.—One of us [12] has shown that the ease of heterolysis of the P–S bond in phosphonothiolates is enormously enhanced by the presence in the system of silver ions, and that fission of N–S bonds (in thionitrites) and C–S bonds (in thiolesters) can be similarly promoted by the use of metal cations possessing high sulphur affinities.[13] These effects are explained on the basis of the metal ion (M^+) co-ordinating with the sulphur atom of a grouping YSZ ($Y =$ an electrophilic group, $Z =$ any univalent group) to produce a *quasi*-sulphonium ion,

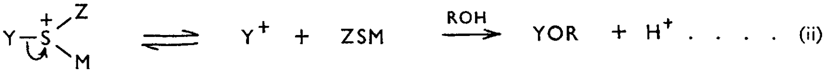
$$Y-S{\scriptstyle\begin{matrix}Z\\ \cdot\end{matrix}}\rightarrow M^+ \longrightarrow Y-\overset{+}{S}{\scriptstyle\begin{matrix}Z\\M\end{matrix}}$$

in which the entity $-S^+MZ$ becomes, heterolytically, a good leaving group relative to $-SZ$. The following kinetically enhanced substitutions thus become possible:



$$X\!: \; Y-\overset{+}{S}{\scriptstyle\begin{matrix}Z\\M\end{matrix}} \longrightarrow \overset{+}{X}-Y + ZSM \quad \cdots\cdots\cdots \text{(i)}$$

where X**:** is any nucleophil (expressed above as a neutral entity), and



$$Y-\overset{+}{S}{\scriptstyle\begin{matrix}Z\\M\end{matrix}} \rightleftharpoons Y^+ + ZSM \xrightarrow{ROH} YOR + H^+ \quad \cdots\cdots \text{(ii)}$$

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[10] Evans, Higgins, Moore, Porter, Saville, Smith, Watson, and Trego, *Chem. and Ind.*, 1960, 897.
[11] Moore and Trego, *Tetrahedron*, 1962, **18**, 305.
[12] Saville, *J.*, 1961, 4624.
[13] Saville, *Analyst*, 1958, **83**, 670.

Equations (i) and (ii) represent in a general way the bimolecular and unimolecular opportunities for nucleophilic substitutions of the *quasi*-sulphonium structure ($Y{\cdot}^{+}SMZ$). Reactions quoted in ref. 12 come into the category of equation (i), and demand the co-operative intervention of nucleophils such as $X\colon$. On the other hand, if the group Y can reasonably exist as a cation then process (ii), akin to the S_N1 reactivity of sulphonium ions, is possible. Inspection of the structures of sulphides previously considered in this paper led to the conclusion that certain of the methylpentenyl groups (II—VI) might well exhibit the constitutional requirements for reactivity according to (ii). In particular, the isoallylic groups (II) and (V), should give rise to well-stabilised carbonium ions, whereas the groups (III), (IV), and (VI) should form carbonium ions much less readily. Hence, conditions might be found such that bonds between sulphur and the groups (II) and (V) could be almost completely broken whereas bonds between sulphur and (III), (IV), and (VI) would remain substantially intact according to reactions of the general kind [$R^1 =$ (II) or (V); $R^2 =$ (III), (IV), and (VI)]:

$$R^1SR^1 + 2Ag^+ + 2H_2O \xrightarrow{\text{fast}} 2R^1OH + 2H^+ + 2Ag_2S \quad . \; . \; . \; . \; . \; . \; . \quad \text{(iii)}$$

$$R^1SR^2 + 2Ag^+ + H_2O \xrightarrow{\text{fast}} R^1OH + H^+ + AgSR^2(Ag^+) \quad . \; . \; . \; . \; . \; . \quad \text{(iv)}$$

$$R^2SR^2 + 2Ag^+ + H_2O \xrightarrow{\text{v. slow}} 2R^2OH, \text{ etc.} + 2H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(v)}$$

It was found that in a large excess of 0·5N-silver nitrate in 75% aqueous ethanol at 22° the sulphides of the kind R^1SR^1 (*e.g.*, XX and XXII) reacted in one hour to 98% completion according to (iii), and a compound of the kind R^1SR^2 (*i.e.*, XXI) reacted to 98% according to (iv), whereas the sulphides (XXV) and (XXVI), typical of the class R^2SR^2 proceeded only to 1·5% of reaction (v) in the same time. These conclusions were based on the acid produced in the reactions and on isolation of unchanged sulphides in partly complete reactions. More critical rate studies suggest that R^1–S bonds are cleaved at about 10,000 times the rate for R^2–S bonds. The analytical value of the above silver ion-assisted solvolysis is as follows: (i) the proportion of groups of the kind (II) or (V) in any mixture of isomeric methylpentenyl sulphides can be determined by measuring the acid liberated on solvolysis in 0·5N-silver nitrate in 75% aqueous ethanol; (ii) if the mixture contains sulphides of the general kind R^2SR^2 [$R^2 =$ (III), (IV), or (VI)] these can be recovered almost quantitatively after solvolysis of other isomers; (iii) the presence of sulphides of the kind R^1SR^2 is revealed by the production of a mixture of silver derivatives of the thiols (X), (XI), and (XIV), *i.e.*, $AgSR^2$. From this mixture the corresponding thiols can be regenerated (see Experimental section) and identified.

These approaches have been used successfully in analyses of actual sulphurations of 2-methylpent-2-ene (forthcoming communication) but we are here primarily concerned with their application in identifying the sulphidic products arising from the interaction of the mixed disulphide (XVIII) and (XIX) with triphenylphosphine.

Formation and Identification of 1,3-*Dimethylbut*-2-*enyl* 1-*Ethyl*-2-*methylallyl Sulphide* (XXXI) *and* 1,1-*Dimethylbut*-2-*enyl* 2-*Methylpent*-2-*enyl Sulphide* (XXIV *and* XXXII).—Treatment of 1,3-dimethylbut-2-enyl 2-methylpent-2-enyl disulphide [70% of (XVIII), 30% of (XIX)] with triphenylphosphine for 75 hours at 80° gave a mixture of di(methylpentenyl) sulphides (isolated in two fractions) in 82% yield. Either fraction on solvolysis in 0·5N-silver nitrate gave exactly one mole of nitric acid per mole of sulphide, a silver mercaptide–nitrate complex, no silver sulphide, and an insignificant unsolvolysed residue. This result clearly demonstrated the absence of symmetrical sulphides of the type R^1SR^1 and R^2SR^2 and the presence in both fractions of only R^1SR^2-type sulphides. The thiols quantitatively regenerated from the silver mercaptides formed on solvolysis of fraction 2 were found by gas–liquid chromatography to consist of 19·5% of (XV) and 80·5% of (XI) and (X), thus describing the R^2 portion of the product.

TABLE 1.

Components of product of interaction 1,3-dimethylbut-2-enyl 2-methylpent-2-enyl disulphide (XVIII and XIX) with triphenylphosphine.

Component No.	Weight % in Fraction 1	Weight % in Fraction 2	R_{x9} *†	Assignment
1	22·0	11·3	7·95	*meso*- and (±)-(XXXI)
2	16·6	10·6	8·89	
3	26·8	29·1	11·83	(XXXII)
4	34·6	49·0	14·15	(XXIV)

* Data for 5% silicone 704 on Celite at 138°.
† See ref. 14 and Experimental.

Gas–liquid chromatographic examination of the monosulphides (Table 1) revealed the presence of four components, only one of which was known from retention data. This (component 4) was sulphide (XXIV) previously observed as the 1,2 addition product in the acid-catalysed treatment of 2-methylpenta-1,3-diene with the thiol (XI). The other three components were assigned to the required compounds having due regard to an expected duplicity of components for (XXXI) since the latter can exist in diastereoisomeric forms [cf. (XX), discussed above].

TABLE 2.

Comparison of estimates of structures (V) and (VI) in the product from treatment of mixture (XVIII) and (XIX) with triphenylphosphine.

	Structure (V) (wt. %) G.L.C. (Table 1)	Structure (V) (wt. %) I.R.	Structure (VI) (wt. %) G.L.C. (Table 1)	Structure (VI) (wt. %) I.R.
Fraction 1	16·1	15·5	25·8	27·2
Fraction 2	9·2	8·1	32·7	32·3

TABLE 3.

Product of addition of thiol mixture * [containing (X), (XI), and (XV)] to 2-methylpenta-1,3-diene.

Component No.	Weight % in Fraction 1	Weight % in Fraction 2	R_{x9} ‡	Assignment
1	13·6	2·7	7·61	(XXXIII)
2	20·9	9·8	8·09	*meso*- and (±)-(XXXI)
3	17·9	10·8	8·76	
4	2·0	1·3	10·16	(XXIII)
5	3·6	3·8	11·88	(XXXII)
6	14·6	21·9	14·16	(XXIV)
7	27·4	50·0	15·50	(XXI)

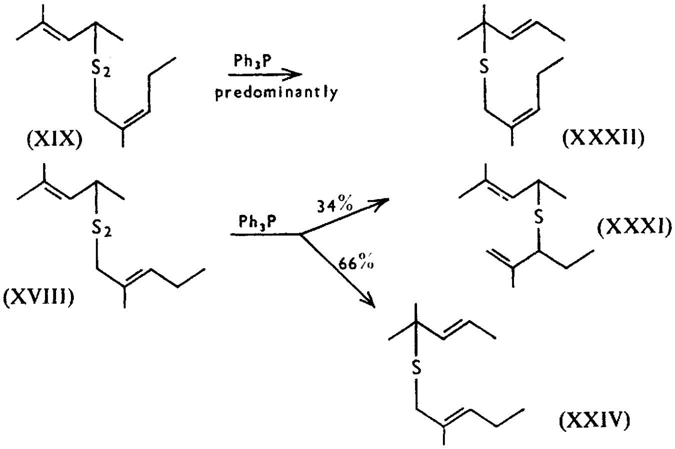
* The mixture contained 37·5% of (XV), 14·0% of (X), and 44·6% of (XI), and the resulting sulphidic product was crudely fractionated into 2 samples.
‡ Refers to 5% silicone 704 on Celite at 138°.

Infrared spectroscopic examination of both fractions confirmed the presence of structures (II), (III) and/or (IV), (V), and (VI). Quantitative estimates of the last two structures are compared in Table 2 with the amounts required according to the assignments given in Table 1. Finally, according to the assignments given in Table 1, the proportion of thiols (X) and (XI) to (XV) expected on silver ion-assisted solvolysis of fraction 2 is 78·2% : 21·8%, in convincing agreement with the proportion found (see above).

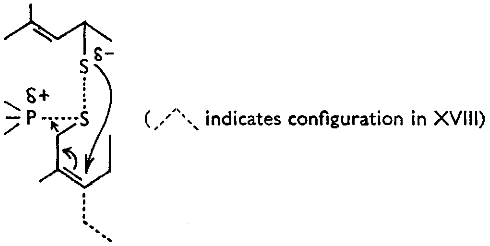
Further confirmation that components 1 and 2 (Table 1) were the *meso* and (±) forms of (XXXI) could be made if a pure sample of thiol (XV) were available since (XXXI) would be the 1,4 product from the acid-catalysed addition of thiol (XV) to 2-methylpenta-1,3-diene. Similarly, if pure thiol (X) were added to the diene under the same conditions, (XXXII) would be the constituent of the binary product corresponding to 1,2 addition. The pure thiols could not be obtained but a mixture of (XV), (X), and (XI) was prepared and added to the diene under acid conditions, giving a sulphide mixture (Table 3), all components of which were expected on the chemical basis [5] of 1,2 and 1,4 additions to the diene.

The " twin " components, 2 and 3 (Table 3), correspond chromatographically with components 1 and 2 (Table 1) assigned as (XXXI) as also does component 5 (Table 3) with component 3 (Table 1) assigned as (XXXII). The validity of the assignments in Table 3 was again substantiated by quantitative infrared spectroscopic analyses.

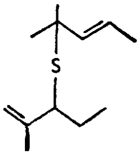
After careful mass-balance considerations, it is concluded that the reactions of the 1,3-dimethylbut-2-enyl *cis*- and *trans*-2-methylpent-2-enyl disulphides [(XIX) and (XVIII)] can be represented as follows:



The different rates of allylic rearrangement of groups (IV) and (III) present respectively in disulphides (XVIII) and (XIX) seem to be ascribable to steric effects. It is suggested that the ethyl group of (XIX), lying in *cis*-juxtaposition to the disulphide group greatly hinders approach of the migrating –S·CH(Me)·CH:CMe$_2$ entity to the double bond in the suggested S_Ni' process.[10,11]



(indicates configuration in XVIII)



(XXXIII)

EXPERIMENTAL

Compounds were examined by both gas–liquid chromatographic and spectroscopic techniques. Where possible, analyses were confirmed by chemical methods (*i.e.*, hydrogenolyses [9] and silver ion-assisted solvolyses). Gas–liquid chromatograms were obtained by using an apparatus previously described [14] employing polyethylene glycol 400, silicone fluid 704, and dinonyl phthalate as stationary phases supported on acid-washed Celite. n-Paraffins were used to determine relative retention times in R_{x9} units.[14]

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[14] Evans and Smith, *J. Chromatography*, 1961, **6**, 293.

Gas–liquid chromatographic examinations of the preparations described below were primarily performed to determine purity. From the data thus obtained there then emerged structure–retention time correlations which were of considerable value in identifying the more complex products. Details of this work will appear elsewhere. Infrared spectra were recorded on a Hilger H.800 double-beam spectrophotometer, a rocksalt prism being used, and quantitative measurements were performed on solutions of the samples in carbon disulphide. Ultraviolet absorption spectra of samples dissolved in cyclohexane were recorded on a Hilger " Uvispek " spectrophotometer. The well-established frequency–structure correlations [15] were used to identify unsaturated groupings, and additional correlations became apparent during this work which proved of value in structural diagnoses.[17]

Materials and Intermediates.—2-Methylpenta-1,3-diene, 4-methylpent-3-ene-2-thiol (IX), 2-methylpentane-2-thiol, and 2-methylpentane-3-thiol were prepared according to Saville's directions.[5] Purified propionaldehyde (6 moles) was added during 15—20 min. to vigorously stirred N-sodium hydroxide (200 ml.) and the resulting organic phase was immediately washed, dried, and distilled to give 80% of 2-methylpent-2-enal (b. p. 136·7°/760 mm., 40·5°/20 mm., n_D^{20} 1·4501) which was reduced [6] with lithium aluminium hydride in ether to 2-methylpent-2-en-1-ol (XIII), isolated in 97% yield by removing solvent from the ethereal extract through an efficient column before distillation of the product. It had b. p. 65°/15 mm., n_D^{20} 1·4453 (Calc. and found: C, 71·9; H, 12·1%); distillation at atmospheric pressure caused dehydration. 1-*Chloro*-2-*methylpent*-2-*ene* (XIV) was made by adding during 1 hr. a mixture of 2-methylpent-2-en-1-ol (XIII) (100 g., 1 mole) and pyridine (22·3 g., 0·28 mole) to phosphorus trichloride (55 g., 0·40 mole) with stirring and rigorous exclusion of moisture. The product was rapidly distilled under reduced pressure, and the distillate washed (ice–water followed by aqueous sodium hydrogen carbonate), dried (potassium carbonate), and redistilled, to give the chloride (60%), b. p. 52—53·5°/41 mm., n_D^{20} 1·4495 (Found: C, 60·6; H, 9·4; Cl, 30·1. $C_6H_{11}Cl$ requires C, 60·8; H, 9·3; Cl, 29·9%. Cl displaced as Cl^- by boiling sodium ethoxide, 29·8%).

2-*Methylpent*-2-*ene*-1-*thiol* (XI). A mixture of thiourea (83·6 g., 1·1 moles), 1-chloro-2-methylpent-2-ene (118·5 g., 1·0 mole), and ethanol (200 ml.) was heated under reflux for 6 hr. About one half of the ethanol was removed under reduced pressure, and the residue was cooled slightly with scratching to induce the crystallisation of S-2-*methylpent*-2-*enylthiuronium chloride* which was isolated by filtration and washing with ethyl acetate. It (146 g., 75% yield based on chloro-olefin) was recrystallised twice by suspension in boiling ethyl acetate (300 ml.), addition of acetic acid in portions until solution was complete, and cooling overnight. The final product (116·8 g., 60%) had m. p. 152—154° (decomp.) (Found: C, 43·2; H, 7·8; S, 16·5. $C_7H_{15}ClN_2S$ requires C, 43·2; H, 7·7; S, 16·5%). The salt (116·5 g., 0·6 mole) was added slowly to a stirred solution of sodium hydroxide (30 g., 0·75 mole) in water (300 ml.) containing a trace of sodium cyanide, and after 2 hr. the resulting organic layer was removed by steam-distillation, washed well with water, and dried (K_2CO_3). Final distillation of the thiol at slightly reduced pressure (to avoid polymerisation which occurs at its atmospheric-pressure boiling point, 146°) yielded fractions (i) b. p. <77·8°/80 mm. (7·63 g.), (ii) b. p. 77·8—78·2°/80 mm. (22·8 g.), and (iii) b. p. 78·2—78·4°/80 mm. (30·1 g.), n_D^{20} 1·4810 (Found: C, 62·1; H, 10·3; S, 27·6. $C_6H_{12}S$ requires C, 62·05; H, 10·35; S, 27·6%), which contained 95% of (XI), 3% of (X), and 2% of (XV). Earlier fractions contained slightly more of (X) and (XV).

Thiol Mixture containing Considerable 2-*Methylpent*-1-*ene*-3-*thiol* (XV).—The mother liquors from the recrystallisation of *S*-2-methylpent-2-enylthiuronium chloride were added to an equal volume of water, and the organic phase was removed. The aqueous layer was then extracted twice with ethyl acetate, once with ether to remove covalent impurities, and then subjected to a nitrogen stream to remove traces of ether. It was then made strongly alkaline with sodium hydroxide, and the resulting organic phase removed by steam distillation. Rapid distillation of the crude thiol (*ca.* 95% of $C_6H_{11}\cdot SH$ by titration [18]) gave a fraction, b. p. mainly 137—141°/760 mm., shown by gas–liquid chromatographic analysis to contain 44·6% of (XI), 14·0% of (X), and 37·5% of (XV), with 3·9% of non-thiol impurities.

Disulphides.—The thiols shown in Table 4 were oxidised [8] in strong aqueous alkali with hydrogen peroxide to yield the corresponding disulphides. The purities of these compounds

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[15] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London.

[16] Smith, "Gas Chromatography," Ed. R. P. W. Scott, Butterworths, London, 1960, p. 114.

[17] Higgins, to be published.

[18] Saville, *Analyst*, 1961, **86**, 29.

as revealed by gas–liquid chromatographic techniques and reductions[9] with lithium aluminium hydride were of the order of 98—100%. The di-(2-methylpent-2-enyl) disulphide (XVII) was a mixture of *cis*- and *trans*-isomers.

TABLE 4.

Thiol	Disulphide		B. p./mm.	n_D^{20}	Found (%) C	H	S
4-Methylpent-3-ene-2-thiol	Bis-(1,3-dimethylbut-2-enyl)	(XVI)	85°/0·05	1·5252	62·8	9·5	27·9 *
2-Methylpent-2-ene-1-thiol	Di-(2-methylpent-2-enyl)	(XVII)	82°/0·001	1·5223	62·9	9·5	28·1 *
2-Methylpentane-2-thiol	Bis-(1,1-dimethylbutyl)		74°/0·005	1·4958	61·55	11·2	27·7 †

* Calc. for $C_{12}H_{22}S_2$: C, 62·6; H, 9·55; S, 27·85%. † Calc. for $C_{12}H_{26}S_2$: C, 61·5; H, 11·1; S, 27·4%.

Mixed Disulphides.—*Ethyl 2-methylpent-2-enyl disulphide.* This was first prepared to establish appropriate experimental conditions for synthesis of 1,3-dimethylbut-2-enyl 2-methylpent-2-enyl disulphide (XVIII): A mixture of sodium thiosulphate hydrate (24·8 g., 0·1 mole) in water (40 ml.) and 1-chloro-2-methylpent-2-ene (11·4 g., 0·096 mole) in ethanol (40 ml.) was heated under reflux (4 hr.) to give a homogeneous solution. Ethanol was distilled off and the aqueous residue freed from some precipitated sulphur and covalent material by extraction with chloroform. A stream of nitrogen was then used to remove traces of chloroform from the aqueous organic thiosulphate solution. A solution of ethanethiol (6·2 g., 0·1 mole) in water (15 ml.) and sodium hydroxide (4·0 g.) was then added to produce an immediate suspension of the mixed disulphide which was isolated by extraction with ether (3 × 40 ml.), and washed with water, followed by drying and distillation of the extracts, to give the disulphide (8·8 g., 50% yield), b. p. 58—59°/0·5 mm., n_D^{20} 1·5180 (Found: C, 54·6; H, 9·2; S, 36·5. $C_8H_{16}S_2$ requires C, 54·55; H, 9·1; S, 36·35%).

1,3-*Dimethylbut*-2-*enyl* 2-*methylpent*-2-*enyl disulphide* (XVIII). Cyclohexylammonium thiosulphate[19] (0·11 mole) was suspended in a mixture of ethanol (40 ml.) and water (20 ml.) at 60°. Freshly prepared 1-chloro-2-methylpent-2-ene (0·10 mole) was added and the mixture shaken to cause rapid dissolution of the salt. After 10 min. at 60° the solution was cooled to 0° and treated with 4-methylpent-3-ene-2-thiol (0·09 mole) in ethanol (40 ml.) containing sodium ethoxide (0·09 mole) during 8 min. with stirring. The mixture was added to water (250 ml.) and acetic acid (6 ml.), then extracted with light petroleum (b. p. 40—60°), and the extracts were washed with water, dried, and distilled to afford the disulphide (40%), b. p. 81—85°/0·001 mm., n_D^{20} 1·5240 (Found: C, 63·05; H, 9·3; S, 27·6. $C_{12}H_{22}S_2$ requires C, 62·6; H, 9·55; S, 27·85%). Infrared spectral analysis confirmed the absence of groupings (V) and (VI) and was consistent with a trialkylethylenic structure for the main component (96% by gas–liquid chromatography), whose retention time agreed exactly with that expected for the unsymmetrical disulphide as calculated[20] from data for (XVI) and (XVII).

Sulphides.—*Additions of unsaturated thiols to* 2-*methylpenta*-1,3-*diene.* These were conducted, essentially according to Saville's method,[5] in the presence of a little 78% perchloric acid in order to obtain substantially pure derivatives containing the 1,3-dimethylbut-2-enyl (II) group. The time of addition of the diene to the thiol–perchloric acid was reduced to 15—30 min. in order to minimise possible acid-catalysed rearrangement of trialkylethylenic to vinylidene groups. This slight modification did not seriously reduce sulphide yields. In this way a number of isomeric sulphides ($C_{12}H_{22}S$ requires C, 72·65; H, 11·2; S, 16·2%) were prepared. *Bis*-(1,3-*dimethylbut*-2-*enyl*) *sulphide* (XX), from the diene (46 ml., 0·40 mole) and 4-methylpent-3-ene-2-thiol (IX) (58 g., 0·50 mole) with perchloric acid (0·4 ml.), had b. p. 66·7—67·3°/0·2 mm., n_D^{20} 1·4866 (Found: C, 72·8; H, 11·1; S, 16·2%). Addition of the mixture of thiols (XI), (X), and (XV) (p. 5052) to the diene, performed on a smaller scale, afforded a sulphide mixture, b. p. 45—50°/0·01 mm. (Found: C, 72·5; H, 11·2; S, 16·2%). Its constitution is outlined in Table 3. 1,3-*Dimethylbut*-2-*enyl* 2-*methylpent*-2-*enyl sulphide* [mainly (XXI)], likewise prepared by using 2-methylpent-2-ene-1-thiol [95% of (XI)], had b. p. 65—68°/0·2 mm., n_D^{20} 1·4900—1·4904 (Found: C, 72·6; H, 11·2; S, 16·3%), and was judged to contain some

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[19] Braithwaite and Graymore, *J.*, 1950, 208.

[20] Evans and Smith, *J. Chromatography*, 1961, **5**, 300.

8—10% of the isomer (XXIV) (cf. 1,2 addition of primary aliphatic thiols and the diene [5]). The sulphide was obtained in rather better isomeric purity (95—96%) by reaction of the sodium derivative of 4-methylpent-3-ene-2-thiol (IX) with 1-chloro-2-methylpent-2-ene according to the general method described below.

Reaction of sodium derivatives of thiols with 1-*chloro*-2-*methylpent*-2-*ene*. To 2·5M-sodium ethoxide in dry ethanol (40 ml.) was added the appropriate thiol (0·11 mole), and the solution was then cooled to 0—5°. The chloro-olefin (11·85 g., 0·10 mole) was added dropwise with stirring during 15 min., and the mixture heated under reflux for 15 min. It was then poured into water, the sulphide being isolated by extraction into ether and distillation. Yields averaged 85%. In this way was prepared 1,3-*dimethylbut*-2-*enyl* 2-*methylpent*-2-*enyl sulphide* [95% pure (XXI)], identical in b. p., R_{x9}, and n_{D}^{20} with the compound prepared by addition of thiol to the diene. *Di*-(2-*methylpent*-2-*enyl*) *sulphide* [mainly (XXV)], b. p. 76—79°/0·8 mm., n_{D}^{20} 1·4923 (Found: C, 72·6; H, 11·3; S, 16·2%), was obtained from 2-methylpent-2-ene-1-thiol and was also prepared from ethanolic sodium sulphide and the chloro-olefin. 1,1-*Dimethylbutyl* 2-*methylpent*-2-*enyl sulphide* (XXIX), likewise prepared by using 2-methylpentane-2-thiol, had b. p. 65—66·5°/0·6 mm., n_{D}^{20} 1·4768—1·4773 (Found: C, 72·1; H, 12·1; S, 16·0. $C_{12}H_{24}S$ requires C, 72·0; H, 12·0; S, 16·0%). 1-*Ethyl*-2-*methylpropyl* 2-*methylpent*-2-*enyl sulphide* (XXX), isomeric with (XXIX), was prepared by using 2-methylpentane-3-thiol and had b. p. 59—60·5°/0·4 mm., n_{D}^{20} 1·4750—1·4759 (Found: C, 71·9; H, 12·0; S, 16·0%).

Reaction of Dialkenyl Disulphides with Triphenylphosphine.—The disulphide (0·1 mole) and the phosphine (0·15 mole) were heated *in vacuo* for certain periods at 80° (cf. Moore and Trego [11]). The liquid part of the product was removed by filtration from triphenylphosphine and triphenylphosphine sulphide which were then washed with a little ether. Distillation of the combined filtrate and washings gave the following dialkenyl sulphides: 1,1-*Dimethylbut*-2-*enyl* 1,3-*dimethylbut*-2-*enyl sulphide* [(97·6% of XXII) containing 2·4% of (XX)] was obtained in 90% yield from the disulphide (XVI) after reaction for 80 hr. It had b. p. 61—62°/1·0 mm., n_{D}^{20} 1·4859 (Found: C, 71·9; H, 11·5; S, 16·6. $C_{12}H_{22}S$ requires C, 72·65; H, 11·2; S, 16·2%). 2—6% of this sulphide is also obtained in preparations of the sulphide (XX). Reaction of the phosphine with di-(2-methylpent-2-enyl) disulphide (XVII) for 40 hr. gave an 82% yield of 1-*ethyl*-2-*methylallyl* 2-*methylpent*-2-*enyl sulphide* [96·8% of (XXVI) and *cis*-analogue], having b. p. 59°/0·03 mm., n_{D}^{20} 1·4859 (Found: C, 72·6; H, 11·2; S, 16·3%), and containing only 3·2% of the isomer (XXV).

A sulphide mixture, M, containing 1,3-dimethylbut-2-enyl 1-ethyl-2-methylallyl sulphide (XXXI) and 1,1-dimethylbut-2-enyl 2-methylpent-2-enyl sulphide (XXIV and XXXII), was obtained in 82% yield through reaction of the mixed disulphide [70% of (XVIII)–30% of (XIX)] (0·1 mole) with triphenylphosphine (0·15 mole) for 75 hr.; it had b. p. 43—45°/0·005 mm., n_{D}^{20} 1·4886 (Found: C, 72·2; H, 11·1; S, 16·0%), and was analysed by gas–liquid chromatography and infrared spectroscopy (Table 1). Confirmation of the constitution of M was gained through application of silver ion-assisted solvolysis, as detailed below.

Silver Ion-assisted Solvolysis of the Mixture M.—The sulphide mixture (0·713 g.) was dissolved in 0·5N-silver nitrate in 75% (v/v) aqueous ethanol (60 ml.), and the solution left at room temperature for 4 hr. A grey-white precipitate of silver mercaptide–silver nitrate complex (S) was then removed by filtration through a bed of Johns-Manville " Hyflo Super-Cel " and was washed with ethanol (3 × 10 ml.) and water (200 ml.). The filtrate and washings were extracted with light petroleum (b. p. 30—40°; 2 × 50 ml.), and the extract was chromatographed on alumina (30 × 1·5 cm.) to remove alcohol and traces of (S), to give an eluate from which solvent was removed by distillation to leave a residue (0·031 g.) of unsolvolysed material containing traces of the sulphides (XXI), (XXV), and (XXVI). The aqueous ethanolic filtrate contained nitric acid equivalent to 36·0 ml. of N/10-sodium hydroxide, determined by titration to a phenolphthalein end-point after addition of pyridine (30 ml.). This acid corresponds exactly with one half of the alkenyl groups in the sulphide sample being either (II) or (V) (see p. 5050). The complex (S) was further examined as follows: it was extracted from the filter-aid by boiling 75% aqueous pyridine (3 × 15 ml.) with rapid hot filtration following each extraction. Addition of water (50 ml.) to the combined filtrates completed the deposition of the yellow silver mercaptides, which were quantitatively isolated by filtration after addition of more filter-aid. When dry, the filter-aid–silver mercaptide mixture was homogenised and a small sample added to a reagent [9] (4 ml.) [composed of thiourea (7 g.), sulphuric acid (3 ml.), water (20 ml.), and tetrahydrofuran (80 ml.)] with vigorous stirring, to give a small upper layer containing thiols corresponding to the silver mercaptide. The layer was increased by adding water (5 ml.) and extracted into light petroleum (b. p. 30—40°; 2 ml.) before analysis by gas–liquid chromatography. The examination revealed only three thiols; (X) and (XI) (80·5% *in toto*) and (XV) (19·5%). Control experiments with synthetic silver mercaptide mixtures made from known mixtures of isomeric thiols had previously confirmed the validity of the analytical method. When the results of the above chemical treatment of M were considered together with instrumental appraisals the assignments of Table 1 followed logically.

THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION,
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