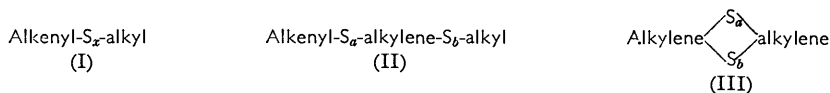


1186. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part XIV.¹ The Reaction of Sulphur and of Dibenzyl Tetrasulphide with 2-Methylpent-2-ene and cis- and trans-3-Methylpent-2-ene*

By C. G. MOORE and M. PORTER

1,3-Dimethylbut-2-enyl 1,1-dimethylbutyl polysulphides (VI; $x > 2$) and 1,1-dimethylbutyl 2-methylpent-2-enyl polysulphides (VII; $x > 2$) are the main products from the reaction of 2-methylpent-2-ene with sulphur at 140°. The same olefin reacts with dibenzyl tetrasulphide to give a mixture of benzyl methylpentenyl sulphides containing mainly trialkylethylenic unsaturation, benzyl methylpentenyl sulphides, and more complex products; benzyl 1,1-dimethylbutyl monosulphide (XIII) is a major product. The structures of these products are consistent with a polar chain sulphuration mechanism involving hydride-ion transfer, similar to that previously advanced to interpret the reaction of trialkylethylenes with sulphur. This mechanism also explains the isomerisation of 2-methylpent-2-ene and *cis*- and *trans*-3-methylpent-2-ene by sulphur and by dibenzyl tetrasulphide at 140° in the dark.

It has been shown previously² that reaction of sulphur with alkenes at about 140° gives mixtures of the three types of sulphide (I)—(III), the relative proportions of which depend chiefly on the degree of substitution at the olefinic double bond. In particular, the principal products from trialkylethylenes are polysulphides (I) in which the unsaturation



pattern (CRR':CHR'') of the olefins is retained and in which the alkyl moieties are exclusively tertiary. The latter structural feature has also been observed in the reaction products of 1-methylcyclohexene with diphenyl tetrasulphide.³ Investigation of the reaction between 2-methylpent-2-ene and dibenzyl tetrasulphide now shows that both features are present in polysulphide-olefin reaction products. Further, by employing gas-liquid chromatography and making use of the recently synthesised methylpentene-thiols⁴ we are now able to give a more detailed description of the products of interaction of 2-methylpent-2-ene with sulphur.

Reaction of 2-Methylpent-2-ene with Sulphur at 140°.—After 5 hours' reaction, small quantities of 2-methylpent-1-ene and volatile sulphur compounds were formed in addition to the main product: involatile "2-methylpent-2-ene polysulphide." Evidence was obtained for the presence of a substance, C₆H₁₀S₂, among the volatile sulphur compounds; this was devoid of thiol groups and had spectroscopic properties consistent with its formulation as (IV) or (V). It may thus be representative of the precursors to the 1,2-dithiole-3-thiones which are formed⁵ by reaction of sulphur with olefins at temperatures above 140°.

¹ Part XIII, C. G. Moore and M. Porter, *Tetrahedron*, 1959, **6**, 10.

² L. Bateman, R. W. Glazebrook, C. G. Moore, M. Porter, G. W. Ross, and R. W. Saville, *J.*, 1958, 2838.

³ G. F. Bloomfield, *J.*, 1947, 1547.

⁴ B. Saville, *J.*, 1962, 5040; M. B. Evans, G. M. C. Higgins, B. Saville, and A. A. Watson, *ibid.*, p. 5045.

⁵ L. Bateman and C. G. Moore in "Organic Sulfur Compounds," Vol. I, ed. N. Kharasch, Pergamon Press, 1961, p. 215, and references there cited.

The spectroscopic properties of "2-methylpent-2-ene polysulphide" and its hydrogenolysis by lithium aluminium hydride to hydrogen sulphide and a mixture of mono- and di-thiols were described in outline in a previous Paper² and are presented in more detail in the Experimental section of this Paper. Gas-liquid chromatography of the



"polysulphide" confirms its polysulphidic nature [<5 wt.-% of mono- and di-sulphides of type (I)] and similar chromatography of the products of its hydrogenolysis for 5 min. at 65° allows the nature and proportions of the derived monothiols to be determined (Table 1).⁶

TABLE 1

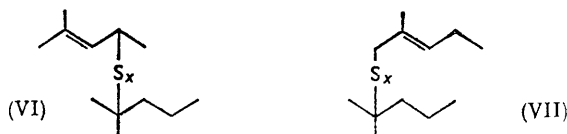
Monothiols produced by hydrogenolysis of "2-methylpent-2-ene polysulphide" with lithium aluminium hydride for 5 min. at 65° in tetrahydrofuran

Thiol	Retention index ⁷	Area (%)
2-Methylpentane-2-thiol	848	50.0
2-Methylpent-3-ene-2-thiol	864	0.8
2-Methylpent-1-ene-3-thiol	890	0.9
4-Methylpent-3-ene-2-thiol	898	34.3
Unidentified	938	1.3
<i>cis</i> -2-Methylpent-2-ene-1-thiol	946	3.5
<i>trans</i> -2-Methylpent-2-ene-1-thiol	955	9.2

The rate of reductive cleavage of S-S bonds by lithium aluminium hydride depends on the nature of the attached groups.⁶ A reaction time of 5 min. at 65° is sufficient to effect complete reduction of di- and poly-sulphides containing substituted allyl groups but may not be sufficient where one or both of the groups is *t*-alkyl (see below). In the present case, effectively complete reduction is achieved after 5 minutes' reaction since 96–99% of the sulphur in the "polysulphide" then appears as hydrogen sulphide and thiol.

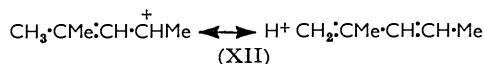
The monothiols listed in Table 1 together represent about 80 mole-% of the hydrocarbon moieties of "2-methylpent-2-ene polysulphide."² Of the remainder, about 15% contain two C-S bonds and will give rise to methylpentanedithiols on hydrogenolysis. These are not eluted from the gas-liquid chromatograms under the conditions used and have not yet been identified.

The results of Table 1 confirm the previously deduced² composition of "2-methylpent-2-ene polysulphide" as largely methylpentenyl methylpentyl polysulphides in which the methylpentenyl groups are tertiary and the methylpentenyl groups contain trialkylethylenic (CRR':CHR'') unsaturation. The methylpentenyl groups are now found to be 2-methylpent-2-enyl ($\text{Me}\cdot\text{CH}_2\cdot\text{CH}:\text{CMe}\cdot\text{CH}_2-$) and 1,3-dimethylbut-2-enyl ($\text{Me}_2\text{C}:\text{CH}\cdot\text{CHMe}-$) in 0.37 : 1 ratio with only trivial amounts of groups containing other types of olefinic unsaturation. The polysulphide is thus to be regarded as consisting, on average, of the polysulphides (VI; $x = 4.55$), 58 mole-% (VII; $x = 4.55$), 22 mole-%; and (III; alkyl-ene = C_6H_{12} , $a + b = 4.55$), 15 mole-%, together with small amounts of other sulphides.



⁶ M. Porter, B. Saville, and A. A. Watson, *J.*, 1963, 346.

⁷ E. Kováts, *Helv. Chim. Acta*, 1958, **41**, 1915; M. B. Evans, *J. Chromatog.*, 1963, **12**, 2.



The reactivity features which lead to addition of a hydride ion to the less substituted carbon atom of the intermediate cyclic persulphonium ion in the reaction sequence shown above have been discussed elsewhere,⁸ as has the formation of polysulphides (such as III) containing more than one C-S bond per hydrocarbon moiety.

Reaction of 2-Methylpent-2-ene with Dibenzyl Tetrasulphide at 140°.—Experiments were carried out for various reaction times using a 6 : 1 molar ratio of olefin to tetrasulphide and the products were separated by vacuum distillation into: (i) a hydrocarbon fraction which consisted largely of 2-methylpent-2-ene together with small amounts of 2-methylpent-1-ene which increased as reaction proceeded (Table 2), and (ii) a residue which consisted of sulphides of general formula $\text{RS}_x\text{R}'$ ($\text{R} = \text{benzyl}$; $\text{R}' = \text{benzyl, methylpentenyl, or methylpentyl}$; $x = 1-3$) and of more complex sulphides. No attempt was made to separate the sulphides from one another or from dibenzyl tetrasulphide except after short reaction times (0—7 hr.) when small quantities of dibenzyl trisulphide were isolated by crystallisation.

The course of the reaction was followed by elemental analysis, molecular-weight determination, and by determining the yields of hydrogen sulphide and thiols formed on reducing the sulphide mixtures with lithium aluminium hydride in boiling tetrahydrofuran for 5 hr. (Table 2). These forcing hydrogenolytic conditions were used to ensure complete reduction of S-S bonds in the sulphides of the types indicated above.⁶ Unfortunately, these conditions also led to the hydrogenolysis of C-S bonds in certain of the reaction products and necessitated corrections for the latter. Corrections were applied to the results of Table 2 on the basis of the fact that benzyl 1,1-dimethylbutyl monosulphide (an important product, see below) under the stated conditions yields hydrogen sulphide (1.7 mole-%) and thiol(s) (13.5 mole-%) and the assumption that all the monosulphides present in the various reaction products behave quantitatively in the same way as benzyl 1,1-dimethylbutyl monosulphide towards lithium aluminium hydride.

The data of Table 2, after correction as described above, are given in the Figure which also indicates the rate of olefin consumption and the formation of species containing monosulphidic sulphur (obtained by difference from total sulphur present and sulphur present in the other two forms).

The Figure shows there is no induction period in the reaction between 2-methylpent-2-ene and dibenzyl tetrasulphide, in contrast to the induction period exhibited by the reaction of the same olefin with sulphur.⁹ This is consistent with the catalytic effect of added polysulphides on olefin-sulphur reactions⁹ and with the mechanism previously proposed for such reactions.⁸ No detailed kinetic analysis of the present results has been attempted but it is apparent that there is initially a rapid conversion of polysulphidic sulphur into di- and mono-sulphidic sulphur but after about 40 hours' reaction this rate becomes slow and nearly independent of time. In this final stage, reacted polysulphidic sulphur reappears solely as monosulphidic sulphur, the concentration of disulphidic sulphur remaining substantially constant at a level slightly below that present initially. The overall reaction involves, very approximately, the conversion of two atoms of polysulphidic sulphur in the tetrasulphide into two atoms of monosulphidic sulphur for the combination of three molecules of olefin. One of these atoms of monosulphidic sulphur is associated with simple monosulphides, $\text{Ph}\cdot\text{CH}_2\cdot\text{S}\cdot\text{R}'$, in which, after 80 hours' reaction, R' is 1,1-dimethylbutyl (see below).

The types of olefinic unsaturation in the involatile products as a function of reaction time were determined by infrared spectrometry (Table 3). The unsaturation pattern is similar to that observed in the "2-methylpent-2-ene polysulphide" obtained by reaction

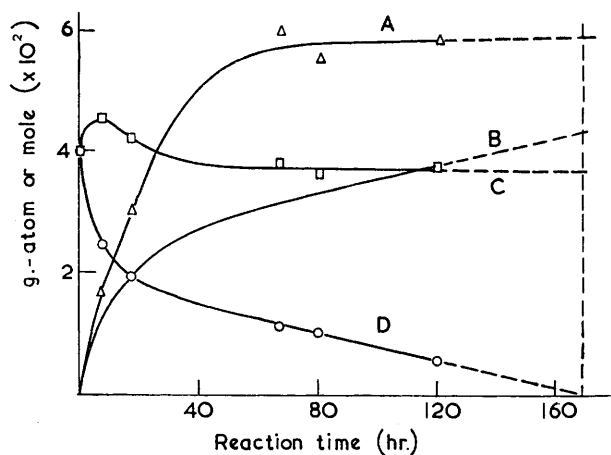
⁹ G. W. Ross, *J.*, 1958, 2856.

TABLE 2

Reaction of dibenzyl tetrasulphide (0.02 mole) with 2-methylpent-2-ene (0.12 mole) at 140°

Reaction time (hr.)	Recovered olefin (g.)	2-Methylpent-1-ene in recovered olefin (g.)	Sulphidic product (g.)	Formula of sulphidic product	Polysulphide sulphur *	Disulphide sulphur *
0	10.11	0.20	6.21	(C _{3.5} H _{3.5} S) _{4.0}	50.1, 47.5 (Calc. 50.0)	53.5, 53.2, 53.9 ‡ (Calc. 50.0)
7	8.71	0.17	7.25	(C _{4.7} H _{6.0} S) _{3.05}	30.4, 34.3 31.6, 33.7	60.5
17	7.55	0.19	8.58	(C _{5.8} H _{8.1} S) _{2.47}	25.8, 24.4	55.8, 58.1
67	5.04	0.38	11.28 †	C _{7.7} H _{12.06} S _{1.80}	14.3	51.4
80	5.42	—	10.90	(C _{7.8} H _{12.2} S) _{1.77}	13.0, 14.1	50.9, 52.2
120	5.16	0.59	11.16 †	(C _{8.26} H _{13.1} S) _{1.63}	8.1	54.1

* Polysulphide sulphur and disulphide sulphur are the percentages of total sulphur present in the sulphidic product which appear as hydrogen sulphide and thiol, respectively, on reduction. † By difference. ‡ The small errors arise from a tendency to over-estimation in the amperometric thiol determinations; corrections for this have not been applied in the Figure.



Olefin consumption and sulphur distribution during the reaction of dibenzyl tetrasulphide (0.02 mole) with 2-methylpent-2-ene (0.12 mole) at 140°. A, olefin consumed; B, monosulphide S; C, disulphide S; D, polysulphide S

TABLE 3

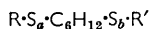
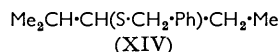
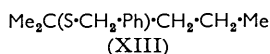
Olefinic unsaturation in sulphidic products from dibenzyl tetrasulphide and 2-methylpent-2-ene

Reaction time (hr.)	Double bonds per molecule of sulphidic product of		
	CRR':CH ₂	<i>trans</i> -CHR':CHR'	CRR':CHR''
5	0—0.05	0—0.06	0.12—0.27
7	0—0.05	0—0.07	0.12—0.27
17	0—0.05	0.02—0.08	0.10—0.25
80	0—0.05	0.03—0.09	0.04—0.19

of 2-methylpent-2-ene with sulphur: the trialkylethylenic (CRR':CHR'') type predominates, but the general level of unsaturation is much lower and symmetrical dialkylethylenic unsaturation is relatively more important. The detailed unsaturation pattern was confirmed in short-path distillates from the sulphidic products (see Experimental section).

Further structural resolution of the sulphidic products was obtained by characterisation of the products of hydrogenolysis. These comprised a mixture of C₆-thiols, toluene- ω -thiol, simple monosulphides, and involatile material containing monosulphide groups. The level of olefinic unsaturation in the C₆-thiols and simple monosulphides was low and decreased with increasing reaction time; after 80 hours' heating it was negligible. The principal C₆-thiol was 2-methylpentane-2-thiol, identified spectroscopically and as its

mercuric mercaptide;¹⁰ 2-methylpentane-3-thiol was not detected. Benzyl 1,1-dimethylbutyl monosulphide (XIII), characterised spectroscopically and as the sulphone, m. p. 86—87°, was the only important simple monosulphidic product. The monosulphide fraction from the 80-hour reaction product was closely examined for the presence of the isomeric benzyl 1-ethyl-2-methylpropyl monosulphide (XIV) as follows: comparison of the infrared spectrum of the fraction with the spectra of synthetic (XIII) and (XIV) indicated a maximum concentration of 5% of the latter; a small proportion of the sulphone was liquid and benzyl 1-ethyl-2-methylpropyl sulphone (m. p. <0°) was identified spectroscopically in amount corresponding to a maximum of 8% of the whole fraction.



(XV; R, R' = benzyl, methylpentenyl, or methylpentyl)

No dithiols were formed on hydrogenolysis, indicating the absence of compounds of type (XV; $a, b > 1$), analogous to those (XV; R, R' = methylpentenyl or methylpentyl, $a, b > 1$) formed on reaction of 2-methylpent-2-ene with sulphur. Analogous monosulphides (XV; $a, b = 1$) cannot be excluded and may have been present among the products of high molecular weight which remained after hydrogenolysis as involatile residues containing only a small proportion of thiol groups.

The above results show that the simple mono-, di-, and poly-sulphidic reaction products have a concentration of olefinic double bonds which is low initially and which is reduced to zero as reaction time is increased to 80 hours. In contrast, but complementary to this, the products of high molecular weight are highly unsaturated as shown by hydrogen : carbon ratios of 1.1—1.3 [*e.g.*, involatile residue from hydrogenolysis after 80 hours' reaction had empirical formula $(\text{C}_{15.2}\text{H}_{17.0}\text{S}_{1.0})_{2.46}$]. Evidently these products contain high proportions of benzyl and/or unsaturated groupings with the 2-methylpentane skeleton. Accurate spectroscopic estimates of double-bond types was not possible because of the complexity of the spectra but more than 0.5 CRR':CHR'' groups per molecule were probably present in the 80-hour product.

The above empirical formula implies that there is insufficient sulphur present to link the C₆ and C₇ units present and hence C—C bond formation must have occurred. This was confirmed by chromatographic separation of the material into several high-molecular-weight fractions having high C₆₋₇ group : S ratios (up to *ca.* 4 : 1). These complex products are not typical of the products from olefin-sulphur reactions at 140° and therefore were not investigated further. They may result as a consequence of special reactivity of benzyl-S linkages¹¹ and/or the long reaction times employed.

The progressive loss of olefinic unsaturation from the simple mono-, di-, and polysulphides during reaction suggests that olefinic centres in initially-formed benzyl methylpentenyl sulphides compete with olefin for reaction with dibenzyl tetrasulphide and other polysulphides, thus forming more complex products. The competitive reaction of equimolar amounts of 2-methylpent-2-ene and benzyl 1,3-dimethylbut-2-enyl monosulphide with a limited quantity of dibenzyl tetrasulphide shows that the unsaturated sulphide reacts 1.5—2.2 times as fast as the olefin. Benzyl methylpentenyl polysulphides may be expected to show the same kind of enhanced reactivity as the monosulphide and hence to be converted preferentially into products of higher molecular weight.

The Mechanism of Reaction of 2-Methylpent-2-ene with Dibenzyl Tetrasulphide.—The two principal structural features of the reaction products of 2-methylpent-2-ene with sulphur, *viz.*, sulphur attachment at the tertiary carbon atom of the methylpentyl moiety

¹⁰ C. G. Moore and R. W. Saville, *J.*, 1954, 2089.

¹¹ D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, 1951, 49, 1; R. W. Saville, *J.*, 1958, 2880, and references there cited.

which compete effectively with reactions (3—4) on the basis of the enhanced reactivity of benzyl 1,3-dimethylbut-2-enyl monosulphide compared with 2-methylpent-2-ene, towards dibenzyl tetrasulphide (p. 6395).

Isomerisation of cis- and trans-3-Methylpent-2-ene by Sulphur and by Dibenzyl Tetrasulphide.—Many sulphur compounds (*inter alia* sulphur dioxide,^{12,13} thiols,^{14,15} thiolacids,¹³ disulphides¹⁶) and sulphur itself¹⁴ catalyse the geometric isomerisation of olefins. Of these isomerising agents, compounds which are capable of giving rise to sulphenyl radicals, *viz.*, thiols and disulphides, are generally only effective in the presence of a source of free radicals or when activated by photolysis or radiolysis. They are believed to act by addition of the sulphenyl radical to the olefinic double bond to form an adduct in which the π -electrons are uncoupled and rotation about the C—C axis is possible; dissociation of the adduct then regenerates the sulphenyl radical and either the *cis*- or the *trans*-isomer of the olefin.

The inability⁸ of simple disulphides (RS₂R; R = alkyl, aralkyl, aryl) to provide sulphenyl radicals by thermal (*non-photolytic*) dissociation at 140° is demonstrated by the extremely slow conversion of *cis*-3-methylpent-2-ene into the *trans*-isomer by diphenyl disulphide at this temperature in the absence of light and oxygen (Table 4), in contrast to the rapid, photochemically-activated, isomerisation of the *cis*-olefin by diphenyl disulphide at room temperature,¹³ when the equilibrium concentration of 64% *trans*-isomer is reached in 18 hours. Quantitative recovery of the disulphide in the non-photolytic experiment points to the absence of any reaction with the olefin in agreement with the conclusion^{3,17} that alkyl, aralkyl, and aryl disulphides are without action on olefins in the dark at temperatures up to 140°.

TABLE 4
Interconversion of *cis*- and *trans*-3-methylpent-2-ene at 140° in the absence of light

Olefin	Reactant	Reaction time (hr.)	Olefin (g.)	Reactant (g.)	Olefin recovered (g.)	Residue (g.)	<i>trans</i> -Isomer recovered (%)	CRR':CH ₂ Isomer recovered (%)
<i>cis</i>	None	48	—	—	—	—	1.0	0.3—0.4
"	Diphenyl disulphide	24	1.37	0.138	1.15	0.137	<4	0.3—0.4
"	Dibenzyl tetrasulphide	24	0.991	0.0908	0.669	0.1481	27—31	1.0
"	Sulphur	5	1.464	0.146	1.06	0.31	20—24	0.4—0.5
"	"	24	0.588	0.0605	0.21	0.18	47 ± 2	2.0
"	"	48	0.749	0.075	0.32	0.21	56—60	1.0
<i>trans</i>	None	48	—	—	—	—	100	0
"	Sulphur	5	0.775	0.0776	0.427	0.32	87—91	0
"	"	24	0.754	0.0751	0.354	0.19	67—72	0.5
"	"	48	0.741	0.0742	0.264	0.20	64—67	0.8—1.0

In contrast with this lack of reactivity, both elemental sulphur and dibenzyl tetrasulphide effect quite rapid interconversion of *cis*- and *trans*-3-methylpent-2-ene at 140° in the dark (Table 4). There is, in addition, a small but definite increase in vinylidene (CRR':CH₂) unsaturation in the olefin which must be ascribed to the formation of 2-ethylbut-1-ene; this is consistent with the formation of small quantities of 2-methylpent-1-ene from 2-methylpent-2-ene during reaction with sulphur (p. 6390) and with dibenzyl tetrasulphide (Table 2). These isomerisations are accompanied by formation of involatile sulphides of the type already described above.

The above *cis*-*trans*-interconversions (and related isomerisations of olefinic rubbers¹⁸)

¹² C. Boelhouwer and H. I. Waterman, *Chem. Weekblad*, 1959, **55**, 465; G. M. Bristow and F. S. Dainton, *Proc. Roy. Soc.*, 1955, **A**, **229**, 525.

¹³ J. I. Cunneen, G. M. C. Higgins, and W. F. Watson, *J. Polymer Sci.*, 1959, **40**, 1.

¹⁴ L. Crombie, *Quart. Rev.*, 1952, **6**, 101.

¹⁵ C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144.

¹⁶ M. A. Golub, *J. Polymer Sci.*, 1957, **25**, 373.

¹⁷ M. Porter, Ph.D. Thesis, London, 1964.

¹⁸ W. A. Bishop, *J. Polymer Sci.*, 1961, **55**, 827; J. J. Shipman and M. A. Golub, *ibid.*, 1962, **58**, 1063.

The formation of 2-methylpent-1-ene from 2-methylpent-2-ene on reaction with sulphur or dibenzyl tetrasulphide can be explained similarly.

EXPERIMENTAL

Materials.—4-Methylpent-3-en-2-one was isolated from commercial mesityl oxide by Stross, Monger, and Finch's method;²⁰ it contained <2% 4-methylpent-4-en-2-one (u.v.). 2-Methylpent-2-ene, prepared by the iodine-catalysed dehydration of 2-methylpentan-2-ol, had b. p. 64—66.6°/736—747 mm., n_D^{20} 1.4000, and contained <2% 2-methylpent-1-ene. *cis*- and *trans*-3-Methylpent-2-ene were prepared and separated as previously described.¹³ Other materials were prepared or purified by standard methods.

General Procedures.—The procedures for hydrogenolysis of polysulphides and determination of thiol sulphur have been described previously.²

Determination of polysulphide sulphur and disulphide sulphur in polysulphides. Polysulphide sulphur and disulphide sulphur are defined as the percentages of total sulphur in the polysulphide liberated as hydrogen sulphide and thiol, respectively, by hydrogenolysis with lithium aluminium hydride. The procedure for their determination was in use prior to that described by Porter, Saville, and Watson⁶ and was similar to that previously described²¹ for the determination of "removable sulphur" except that 2*N*-nitric acid was used to liberate the hydrogen sulphide; the total liquid products were then made up to standard volume with ethanol and thiol determinations were carried out on aliquot portions of this solution to give the disulphide-sulphur content.

Molecular weights were determined ebullioscopically in benzene unless stated otherwise.

Spectrometric analysis. Infrared spectra were recorded on a Hilger H.800 spectrometer or on a Grubb-Parsons single-beam instrument. Ultraviolet absorption spectra were determined in cyclohexane solution with a Hilger Uvispek spectrophotometer. Olefinic unsaturation in sulphides was estimated with reference to the following standards: for CRR'·CH₂ type, 2,4,4-trimethylpent-1-ene; for *trans*-CHR'·CHR', *trans*-but-2-enyl methyl sulphide; for CRR'·CHR'', benzyl 1,3-dimethylbut-2-enyl monosulphide in the experiments with dibenzyl tetrasulphide, and 2-methylpent-2-ene in the experiments with sulphur. Maximum values were obtained by simple application of these standards but, where the sulphides under examination were predominantly saturated, minimum values were obtained by first subtracting an average value for the absorption of a number of saturated benzyl mono- and poly-sulphides at the relevant wavelengths. Phenyl groups were estimated similarly from the relatively sharp absorption bands at 1030 and 1070 cm.⁻¹, using average standards obtained from the same saturated benzyl sulphides. The method used for the determination of *cis*- and *trans*-3-methylpent-2-ene has been described by Cunneen, Higgins, and Watson.¹³

Synthesis of Reference Compounds.—*Benzyl 1,1-dimethylbutyl sulphide.* This sulphide, b. p. 78—79°/0.1 mm., n_D^{20} 1.5241, was prepared in 86% yield by polar addition of toluene- ω -thiol to 2-methylpent-2-ene.¹⁰ It was oxidised by peracetic acid to *benzyl 1,1-dimethylbutyl sulphone*, colourless needles, m. p. 86—87° [after four-fold crystallisation from light petroleum (b. p. 60—80°)] (Found: C, 65.0; H, 8.65; S, 13.2. C₁₃H₂₀O₂S requires: C, 65.0; H, 8.35; S, 13.35%).

2-Methylpentane-2-thiol. This thiol and its mercury mercaptide, m. p. 75.5—76.5°, were prepared from the above sulphide.¹⁰

Benzyl 1-ethyl-2-methylpropyl sulphide. Reaction of toluene- ω -thiol (12.4 g., 0.1 mole) with 2-methylpent-2-ene (8.4 g., 0.1 mole) for 7 hr. *in vacuo* under illumination from a 500-w ultra-violet lamp gave a poor yield (3.4 g., 16%) of the sulphide. An increased yield (*ca.* 25%) was obtained by adding a few drops of chenopodium oil (86% ascaridole) and illuminating for 21 hr. Fractionation of the products afforded *benzyl 1-ethyl-2-methylpropyl sulphide* as a colourless liquid, b. p. 78.5—80°/0.1 mm., n_D^{20} 1.5252 (Found: C, 75.1; H, 9.7; S, 15.3. C₁₃H₂₀S requires: C, 75.0; H, 9.6; S, 15.4%). The *sulphone*, obtained by peracetic acid oxidation, was a colourless liquid, only partially purified by distillation at 10⁻³ mm. (bath temp. 120—130°) (Found: C, 66.3, 66.35; H, 8.8, 8.65; S, 13.5. C₁₃H₂₀O₂S requires: C, 65.0; H, 8.35; S, 13.35%).

Benzyl 1,3-dimethylbut-2-enyl sulphide. A solution of 4-methylpent-3-en-2-one (49.0 g.,

²⁰ F. H. Stross, J. M. Monger, and H. de V. Finch, *J. Amer. Chem. Soc.*, 1947, **69**, 1627.

²¹ E. H. Farmer, J. F. Ford, and J. A. Lyons, *J. Appl. Chem.*, 1954, **4**, 554.

0.5 mole) in anhydrous ether (120 ml.) was added dropwise to a well-stirred suspension of lithium aluminium hydride (10.0 g., 0.025 mole) in anhydrous ether (400 ml.) over 4 hr. Decomposition of the complex by water (25 ml.) followed by aqueous 1N-sulphuric acid (100 ml.), separation of the ether layer and further extraction with ether afforded a combined extract from which a main fraction, b. p. 50.0—50.2°/23 mm. (36.65 g.) was obtained by distillation. This, united with a similar fraction from a second experiment, was refractionated to give 4-methylpent-3-en-2-ol, b. p. 49—50°/19 mm. (66.8 g., 67%) (Found: C, 72.05; H, 12.1. Calc. for $C_8H_{12}O$: C, 71.95; H, 12.1%). The ultraviolet spectrum indicated the absence of the unsaturated ketone and the conjugated diene (but see ref. 22); 2-methylpent-3-en-2-ol was probably present²³ but this is not important since the bromide (see below) is tautomeric.

The unsaturated alcohol was converted into the corresponding bromide, b. p. 51—57°/35—43 mm. (63%), by the method of Rouvé and Stoll.²⁴ The bromide (34.4 g., 0.21 mole) was added slowly to a cooled stirred solution of sodium benzyl mercaptide [prepared by adding toluene- ω -thiol (26.2 g.) in benzene (50 ml.) to sodium (5.0 g.) in ethanol (130 ml.)] under nitrogen and the mixture warmed to 40° over 0.5 hr. and set aside for 2 days. The precipitated sodium bromide was filtered off, the solvent distilled off at low pressure, and the residue poured into water (300 ml.) which was then neutralised with hydrochloric acid. Extraction with benzene gave, after two fractionations, *benzyl 1,3-dimethylbut-2-enyl sulphide*, a colourless liquid, b. p. 76—77°/0.07 mm. (25.6 g., 59%) (Found: C, 75.5; H, 8.75; S, 15.5. $C_{13}H_{18}S$ requires: C, 75.65; H, 8.8; S, 15.55%). A band at 852 cm^{-1} (ϵ 51) in the infrared spectrum was assigned to the C-H deformation vibration of a CRR':CHR' grouping. Unsaturation of the type CRR':CH₂ was absent but a definite conclusion concerning the *trans*-CHR:CHR'-group content could not be reached since the assignment of a band at 970 cm^{-1} to the C-H deformation vibration of this grouping could not be made with certainty; if due to *trans*-CHR:CHR' groups, such an assignment would indicate the presence of 0.12 double bonds per molecule of this type. The identity of the product was clarified by a study of its rate of reaction with perbenzoic acid in benzene²⁵ by which it was shown to be benzyl 1,3-dimethylbut-2-enyl sulphide containing $6 \pm 2\%$ of the isomeric benzyl 1,1-dimethylbut-2-enyl sulphide.

Reactivity of Benzyl 1,1-Dimethylbutyl Sulphide towards Lithium Aluminium Hydride.—Determinations of polysulphide sulphur and disulphide sulphur on benzyl 1,1-dimethylbutyl sulphide gave results of 1.3, 1.7, 1.6, 2.3, and 13.55, 13.5%, respectively. Large-scale hydrolysis of the sulphide (4.165 g.) with lithium aluminium hydride (0.523 g.) gave the following fractions: (i) mixture of solvent and a thiol (contents of a trap at 0.1 mm.) (Found: thiol-S equivalent to 0.020 g. C_8 -thiol); (ii) unchanged sulphide, b. p. 83—84°/0.1 mm. (3.401 g.) (Found: C, 74.45; H, 9.75; S, 15.8; thiol S, 0.09. Calc. for $C_{13}H_{20}S$: C, 75.0; H, 9.6; S, 15.4%); (iii) a residue (0.333 g.) (Found: C, 75.2; H, 9.35; S, 15.3%; *M*, 215, 238). Recovery was 90%.

Reaction of 2-Methylpent-2-ene with Sulphur.—A mixture of the olefin (100.0 g.) and sulphur (10.0 g.) was heated *in vacuo* at $140 \pm 0.1^\circ$ for 5.0 hr. An insignificant amount of sulphur crystallised out at -20° . Evaporative distillation of a portion (109.71 g.) of the product at $<50^\circ/10^{-4}$ mm. gave (i) 2-methylpent-2-ene, n_D^{20} 1.4009 (87.15 g.) (Found: C, 85.7; H, 14.7; S, $<0.1\%$), spectroscopically identical with the starting material but for a slight increase in CRR':CH₂ groups; (ii) a volatile product, n_D^{20} 1.5070 (2.00 g.) [Found: C, 56.25; H, 9.1; S, 34.4; thiol S, 0.2%; *M*, 220, 192. Corresponds to $(C_6H_{11.6}S_{1.4})_{1.75}$]; and (iii) "2-methylpent-2-ene polysulphide," n_D^{20} 1.577 (20.20 g.) [Found: C, 47.0, 47.2; H, 7.95, 7.8; S, 45.3, 45.45; polysulphide S, 50.7, 51.8%; *M*, 314, 319. Corresponds to $(C_6H_{12.0}S_{2.18})_{2.06}$]. The infrared spectrum of (ii) was similar to that of (iii), except for the presence of a medium-intensity band at *ca.* 780 cm^{-1} in the former. The infrared spectrum of (iii) was very similar to that of synthetic bis-1,1-dimethylbutyl polysulphide¹⁰ between 1500 and 700 cm^{-1} ; in particular, strong bands at 1158, 1132, and 740 cm^{-1} , characteristic of the 1,1-dimethylbutylthio-group, correspond in intensity to the presence of 1.07, 1.00, and 1.08 such groups per molecule, respectively. Unsaturation was mainly of CRR':CHR' type but bands near 890 and 960 cm^{-1} where CRR':CH₂ and *trans*-CHR:CHR' type, respectively, would be expected to absorb, were also present in similar intensity in the spectrum of bis-1,1-dimethylbutyl polysulphide and

²² J. Knights and E. S. Waight, *J.*, 1955, 2830.

²³ M. E. Cain, *J.*, 1964, 3532.

²⁴ A. Rouvé and M. Stoll, *Helv. Chim. Acta*, 1947, **30**, 2216.

²⁵ C. G. Moore and M. Porter, forthcoming publication.

identification of these double bond types is therefore doubtful; maxima of 0.06 and 0.05 double bonds per molecule, respectively, could be present.

[With Dr. G. W. Ross]. A volatile fraction, corresponding to (ii), from a similar experiment gave, on refractionation, 2-methylpent-2-ene and two yellow fractions: (iia) (0.56 g.) [Found C, 63.55; H, 10.35; S, 26.8; thiol S, 2.4%; M (cryoscopic in benzene), 125. Calc. for 39 wt.-% C_8H_{12} and 61 wt.-% $C_8H_{10}S_2$: C, 63.5; H, 9.8; S, 26.8%; M , 122.5]; and (iib) (1.78 g.) [Found: C, 53.1; H, 8.3; S, 37.9; thiol S, 1.9%; M (cryoscopic in benzene), 115. Corresponds to $(C_8H_{11.1}S_{1.6})_{0.86}$]. The infrared spectrum of (iia) confirmed the presence of 2-methylpent-2-ene (30–50%) and bands at 1632 and 1560 cm^{-1} were ascribed to additional C:C stretching vibrations. Splitting of the symmetrical CH_3 deformation band indicated the presence of *gem*-dimethyl groups and a medium-intensity band at *ca.* 780 cm^{-1} could be due to a sulphurated CRR':CHR' grouping. An inflection in the ultraviolet spectrum at *ca.* 235 $m\mu$, $E_{1\%}^{1cm}$, 100, characteristic of an isolated C:C-S chromophore, was observed. Fraction (iib) was spectroscopically similar but showed only a shallow inflection at 235 $m\mu$ ($E_{1\%}^{1cm}$, 44) and contained unsaturation of CRR':CH₂ type in addition to CRR':CHR'.

Hydrogenolysis of "2-Methylpent-2-ene Polysulphide."—Hydrogenolysis of fraction (iii) (8.420 g.) with lithium aluminium hydride (5.0 g.) gave: (iv) mainly solvent (10.51 g.) (Found: thiol S, 0.54%); (v) a mixture of thiols and tetrahydrofuran, n_D^{20} 1.4406 (2.53 g.) (Found: C, 62.6, 62.7; H, 11.2, 11.3; S, 21.2, 21.35; thiol S, 22.8%), collected in a trap; (vi) a monothiol fraction, b. p. 22–29°/23 mm., n_D^{20} 1.4533 (1.17 g.) (Found: C, 62.6; H, 11.3; S, 25.8; thiol S, 27.6. Calc. for $C_8H_{10}S$: C, 62.0; H, 10.4; S, 27.6. Calc. for $C_8H_{14}S$: C, 61.0; H, 11.9; S, 27.1%); containing, from its infrared spectrum, 2-methylpentane-2-thiol and 0.5 CRR':CHR' groups per molecule (assuming M , 120) but negligible 2-methylpentane-3-thiol or CRR':CH₂ groups; (vii) a monothiol-dithiol mixture, b. p. 37–40°/23 mm. (0.21 g.) (Found: C, 60.15, 60.65; H, 10.55, 10.3; S, 28.6; thiol S, 29.4%; M , 170); (viii) a predominantly (saturated) dithiol fraction, b. p. 75–80°/23 mm., n_D^{20} 1.5003 (1.32 g.) (Found: C, 50.25, 50.45; H, 9.5, 9.6; S, 39.5, 39.8, 40.0; thiol S, 38.7%; M , 160, 166. Calc. for $C_8H_{14}S_2$: C, 48.0; H, 9.4; S, 42.7, thiol S (2SH), 42.7%; M , 150) giving a stable green coloration with aqueous manganous acetate in the presence of pyridine, diagnostic of a *vic*-dithiol;²⁶ and (ix) a residue, n_D^{20} 1.5149 (0.50 g.) [Found: C, 61.2; H, 10.7; S, 27.6; thiol S, 11.2%; M , 261. Corresponds to 26 wt.-% $C_8H_{12}(SH)_2$, 74 wt.-% non-thiol of formula $(C_8H_{12.1}S_{0.76})_{3.24}$] containing, from the intensities of infrared bands at 977, 898, and 848 cm^{-1} , respectively, 0.17 *trans*-CHR:CHR', 0.11 CRR':CH₂, and 0.4–0.5 CRR':CHR' groups per molecule.

A polysulphide fraction (0.178 g.) [Found: C, 46.1, 46.1; H, 7.8, 7.6; S, 46.4, 46.3; polysulphide S, 48.1, 47.3; disulphide S (method of ref. 6), 51.3, 48.5%; M , 298, 312. Corresponds to $(C_8H_{11.94}S_{2.26})_{1.95}$] similar to (iii) was hydrogenolysed using the method of ref. 6 and the thiols were examined in light petroleum solution by gas-liquid chromatography on a 20% dinonyl phthalate/Celite column at 65°. The thiols were identified by comparison of their retention indices (relative to hexane-1-thiol as internal standard) with those of authentic samples^{4,10} and estimated from the relative peak areas (Table 1).

Reaction of 2-Methylpent-2-ene with Dibenzyl Tetrasulphide.—The following experiment was typical of those performed for various reaction times, the results of which are summarised in Tables 2 and 3 and in the Figure. The tetrasulphide (6.21 g., 0.02 mole) and the olefin (10.10 g., 0.12 mole) were heated together *in vacuo* in the dark at 140° for 7.0 hr. Bulb-to-bulb distillation of the products at <50°/ <10⁻³ mm. gave (i) 2-methylpent-2-ene (8.50 g.) (Found: S, 0.15; thiol-S, 0.05%); (ii) a yellow volatile fraction (0.22 g.) (Found: S, 7.85, 8.1; thiol S, 1.2, 2.1%), mostly 2-methylpent-2-ene but containing a substance with phenyl groups; (iii) a residual dark red-brown liquid "polysulphide" (7.25 g.) [Found: C, 59.4, 59.4; H, 6.4, 6.4; S, 33.8, 33.7; thiol S, 0.1; polysulphide S, 30.4, 34.3, 31.6, 33.7; disulphide S, 60.5%; M , 290, 286. Corresponds to $(C_{4.7}H_{6.0}S_{1.0})_{3.05}$], which deposited colourless plates of dibenzyl trisulphide, m. p. 48–49° (from ethanol) (Found: C, 60.4; H, 5.2; S, 34.5. Calc. for $C_{14}H_{14}S_3$: C, 60.4; H, 5.05; S, 34.55%) leaving a liquid fraction which was shown spectroscopically to be largely saturated with 0.12–0.27 double bond per molecule of CRR':CHR' type, 0–0.07 double bond of *trans*-CHR:CHR' type, and 0–0.05 double bond of CRR':CH₂ type. Phenyl groups were estimated at 1.35, 1.34 per molecule. The ultraviolet absorption spectrum was similar to that of dibenzyl trisulphide.

Hydrogenolysis.—The polysulphide fraction (20.00 g.) corresponding to (iii) above, obtained

²⁶ D. H. Rosenblatt and G. N. Jean, *Analyt. Chem.*, 1955, **27**, 951.

after heating for 80 hr., gave the following fractions after treatment with lithium aluminium hydride: (iv) recovered light petroleum, b. p. $<60^{\circ}/760$ mm. containing a C_6 -thiol (0.865 g.); (v) contents of a trap at 42 mm. (4.570 g.) (thiol S corresponds to 0.510, 0.516 g. C_6 -thiol); (vi) b. p. $30-40^{\circ}/42$ mm. (1.698 g.) (Found: C, 63.15; H, 10.85; S, 26.15; thiol S, 29.3, 28.7, 29.2%; C:H, 1:2.05. Calc. for $C_6H_{14}S$: C, 60.95; H, 11.9; S, 27.1. Calc. for $C_6H_{12}S$: C, 62.0; H, 10.4; S, 27.6. Calc. for C_7H_8S : C, 67.7; H, 6.5; S, 25.75%); (vii) b. p. $23-31^{\circ}/0.1-0.2$ mm. (2.777 g.) (Found: C, 66.2; H, 8.2; S, 25.8; thiol S, 22.9, 23.1%; C:H, 1:1.48); (viii) intermediate fraction (0.234 g.) (Found: C, 73.15; H, 10.3; S, 16.6%); (ix) b. p. $84-88^{\circ}/0.1-0.2$ mm. (6.364 g.) (Found: C, 74.8; H, 9.6; S, 15.9, 16.0; thiol S, 0.7%; M , 207, 206. Calc. for $C_{13}H_{20}S$: C, 75.0; H, 9.6; S, 15.4%; M , 208); (x) b. p. $90-100^{\circ}/0.1-0.2$ mm. (1.142 g.) [Found: C, 74.3; H, 8.7; S, 17.15; thiol-S, 2.4, 2.7%; M , 219, 224; C:H, 1:1.40. Corresponds to $(C_{11.6}H_{16.1}S_{1.0})_{1.18}$]; and (xi) a dark residue (2.622 g.) [Found: C, 78.8; H, 7.4; S, 13.85; thiol S, 2.0%; M , 578, 560; C:H, 1:1.12. Corresponds to $(C_{15.2}H_{17.0}S_{1.0})_{2.46}$].

Examination of the hydrogenolysis fractions. No unsaturation could be detected in fraction (iv) or (v). Fraction (vi) was identified as being mainly 2-methylpentane-2-thiol by spectroscopic comparison with the synthetic material and by preparation of the mercuric mercaptide, m. p. and mixed m. p. $75.5-76.5^{\circ}$ (Found: C, 32.85; H, 6.25. Calc. for $C_{12}H_{26}S_2Hg$: C, 33.1; H, 6.0%). A small amount of olefinic unsaturation, probably $CRR':CHR''$, and a trace of toluene- ω -thiol were present; the presence of 2-methylpentane-3-thiol was unlikely. Fraction (vii) contained 50-60 mole-% toluene- ω -thiol and probably 2-methylpentane-2-thiol but apparently no unsaturated component. Spectroscopic comparison of fraction (ix) with benzyl 1,1-dimethylbutyl sulphide and benzyl 1-ethyl-2-methylpropyl sulphide showed it to be almost entirely the former compound with a maximum of 5% of the latter. There was no unsaturation. Peracetic acid oxidation of fraction (ix) (2.08 g.) gave benzyl 1,1-dimethylbutyl sulphone (1.74 g., 73%), m. p. $86.5-88^{\circ}$, mixed m. p. $86-87.5^{\circ}$ (Found: C, 64.9; H, 8.4; S, 13.35. Calc. for $C_{13}H_{20}S_2$: C, 65.0; H, 8.35; S, 13.35%) and a mixture of solid and liquid sulphones (0.44 g.) (Found: C, 65.4, 65.4; H, 8.6, 8.7; S, 12.9, 12.85%) in which benzyl 1-ethyl-2-methylpropyl sulphone was shown spectroscopically to be present in a maximum concentration of 40%, representing 8% of the sulphone formed. Fraction (x) was mainly saturated with 0.10-0.15 double bonds per molecule of $trans\text{-}CHR':CHR'$, 0-0.17 double bonds of $CRR':CHR''$, and 0-0.08 double bonds of $CRR':CH_2$ type. Phenyl groups were estimated at 1.2, 0.95 groups per molecule. Similar estimates of unsaturation on fraction (xi) gave results of 0.57-0.72 $CRR':CHR''$, 0.20-0.26 $trans\text{-}CHR':CHR'$, and 0.15-0.20 $CRR':CH_2$ type double bonds per molecule but are likely to be unreliable because of the high molecular weight and unknown nature of the material. With a similar reservation, there were 3.9, 2.8 phenyl groups per molecule. The fraction was separated by extraction with light petroleum (b. p. $60-80^{\circ}$) and chromatography on alumina into eleven, mostly very small fractions, the largest of which were: (xi a) orange mobile oil [Found: C, 79.5, 79.6; H, 11.2, 11.25; S, 7.55, 7.7%; M , 352, 340. Corresponds to $(C_{27.6}H_{46.5}S_{1.0})_{0.84}$] which contained 0.08-0.22 double bonds of $CRR':CHR''$, 0.03-0.07 double bonds of $CRR':CH_2$, 0.11-0.17 double bonds of $trans\text{-}CHR':CHR'$ type, and 1.2, 0.94 phenyl groups per molecule. The ultraviolet spectrum was incompatible with the presence of 1,2-dithiole-3-thione groups and of substituted thiophen groupings; (xi b) a red-brown oil [Found: C, 75.2; H, 7.9; S, 15.0%. Corresponds to $(C_{13.4}H_{16.8}S_{1.0})_n$] with similar amounts of olefinic unsaturation but containing 2.2, 1.65 phenyl groups per molecule; (xi c) a red-brown oil (Found: C, 75.95; H, 8.1; S, 11.8%); (xi d) a red-brown viscous oil [Found: C, 78.5; H, 7.4; S, 13.3%. Corresponds to $(C_{15.8}H_{17.7}S_{1.0})_n$]; (xi e) a dark brown amorphous solid [Found: C, 81.15; H, 6.75; S, 12.4%. Corresponds to $(C_{17.5}H_{17.3}S_{1.0})_n$]; (xi f) a dark brown gum (Found: C, 77.4; H, 6.9; S, 9.9%).

Molecular Distillation of the "Polysulphidic" Products.—Molecular distillation of the 80-hr. reaction product (1.421 g.) at $35^{\circ}/10^{-3}$ mm. gave a deep yellow distillate (0.861 g.) (Found: C, 69.1; H, 9.75; S, 21.1%; M , 212, 227, 222, 208) which, from its infrared spectrum, was benzyl 1,1-dimethylbutyl sulphide (Calc. for $C_{13}H_{20}S$: C, 75.0; H, 9.6; S, 15.4%; M , 208), but which contained *ca.* 20 mole-% of material with a higher sulphur content, possibly a benzyl methylpentyl trisulphide, on the basis of its elemental analysis and polarographic behaviour.

Similar distillation of a product (2.711 g.) obtained after a 5-hr. reaction period (and from which unreacted olefin and much dibenzyl trisulphide had been removed) gave a pink liquid distillate (0.843 g.) [Found: C, 65.8; H, 8.6; S, 25.1%; M , 212, 214. Corresponds to $(C_{13.0}H_{20.2}S_{1.86})_{0.90}$] and a deep red residue (1.783 g.) [Found: C, 56.5, 56.25; H, 6.3, 6.3; S,

37.0, 37.3%; M , 291, 293. Corresponds to $(C_{4.05}H_{5.39}S_{1.00})_{3.39}$. The infrared spectrum of the distillate was similar to that of benzyl 1,1-dimethylbutyl sulphide but the presence of 0.11—0.26 $CRR''CHR''$, 0—0.05 $CRR'CH_2$, 0.02—0.08 *trans*- $CHR:CHR'$ -type double bonds per molecule was indicated, as well as 0.87, 0.91 phenyl groups. Polarographic examination showed the distillate to be a 50 : 50 wt.-% mixture of mono- and tri-sulphides.

Competitive Reaction of 2-Methylpent-2-ene and Benzyl 1,3-Dimethylbut-2-enyl Sulphide with Dibenzyl Tetrasulphide at 140°.—A mixture of the tetrasulphide (10.317 g., 0.033 mole), olefin (4.187 g., 0.05 mole), and the monosulphide (10.303 g., 0.05 mole) was heated *in vacuo* in the dark for 7.0 hr. at 140°. The volatile products (3.388 g.) were separated by distillation at atmospheric pressure into unreacted olefin (2.911 g.), spectroscopically identical with 2-methylpent-2-ene, and a small residue (0.278 g.). Half (10.69 g.) of the involatile residue, subjected to flash heating to 100—125° at 0.1 mm. for 50 min., gave a yellow fraction, b. p. 76—82°/0.1 mm. (3.140 g.) [Found: C, 74.1; H, 9.1; S, 16.6%; M , 228, 223. Calc. for $C_{13}H_{18}S$: C, 75.65; H, 8.8; S, 15.55%; M , 206. Calculated as a mixture of $C_{13}H_{18}S$ and $C_{13}H_{18}S_2$, corresponds to 84—91 wt.-% $C_{13}H_{18}S$] which was identified by its infrared spectrum as mainly benzyl 1,3-dimethylbut-2-enyl sulphide with 0.8—0.9 double bonds per molecule of $CRR''CHR''$ and 0—0.05 double bonds per molecule each of $CRR'CH_2$ and *trans*- $CHR:CHR'$ type. The ultraviolet spectrum showed the absence of the C:C:S chromophore.

Isomerisation Experiments with 3-Methylpent-2-ene (Table 4).—The olefin and the reactant (weights as shown in Table 4) were thoroughly degassed and heated *in vacuo* in the dark at 140° for the times indicated. The olefinic products were separated from reactant and any sulphurated products by rapid distillation, and examined spectroscopically. Care was taken to exclude light, both during the heating period and in all subsequent operations. The recovered olefin samples were devoid of sulphurated material and, in the case of the experiment with the polysulphide, of phenyl groups. In the experiment with diphenyl disulphide, the residue (0.137 g., 100% recovery) after olefin removal had m. p. and mixed m. p. (with diphenyl disulphide), 59—60°.

Infrared-spectroscopic examination of the polysulphidic residue from reaction of *cis*-3-methylpent-2-ene with sulphur for 5 hr. at 140° showed the presence of $RR'C:CHR''$ -type unsaturation but the amount could not be determined owing to the small quantity of material available; a maximum of 5% of the total olefinic unsaturation could have been of $RR'C:CH_2$ type and the $RCH:CH_2$ type was absent.

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