591. *Oxidation of Organic Sulphides. Part VII.* The Mechanism of Autoxidation of But-2-enyl Methyl Sulphide, Methyl 1-Methylbut-2-enyl Sulphide, and* n-*Butyl Methyl Sulphide.*

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The products of autoxidation of the sulphides named in the title have been identified and estimated quantitatively. The relative proportions of sulphoxide, water, and dimethyl disulphide vary widely. The yield of sulphoxide is independent of the extent of oxygen absorption in the saturated sulphide, but decreases as reaction proceeds with the allylic sulphides, markedly so with the dimethylallyl methyl sulphide.

These and related observations can be correlated on the basis of a reaction mechanism comprising (1) a free-radical chain reaction producing a hydroperoxido-sulphide, (2) interaction of this compound with the original sulphide to form sulphoxide and hemithioacetal, and (3) decomposition of the hemithioacetal and, in the unsaturated sulphide systems, the sulphoxide. The extent and nature of the last stage appear responsible for the major differences in the three systems. A reaction mechanism incorporating these features and consistent with other data on autoxidation reactions and hydroperoxide–sulphide interactions is presented.

Attempts to prepare but-2-enal dimethyl thioacetal always gave the isomeric 1 : 3-dimethylthiobut-1-ene.

Allylic sulphides react with oxygen at first autocatalytically, then at an apparently steady rate which soon decreases and, in general, gives way to auto-inhibition when only a small fraction of a mol. of oxygen has been absorbed.[1] Only for *cyclo*hex-2-enyl methyl sulphide have the products of reaction been investigated.[2] This work has now been extended to allylic acyclic sulphides, which more nearly resemble ordinary vulcanized rubber,[3] where such reactions are of great technological importance.

* Part VI, Hargrave, *Proc. Roy. Soc.*, 1956, *A*, **235**, 55.

[1] Bateman and Cunneen, *J.*, 1955, 1596.

[2] Bateman and Shipley, *J.*, 1955, 1996.

[3] Bateman, Glazebrook, Moore, and Saville, Proc. 3rd Internat. Rubber Tech. Conf., London, 1954, p. 298.

But-2-enyl methyl sulphide, selected first for detailed study, reacts less readily than the *cyclo*hexenyl analogue, and absorbs about 5 mol. % of oxygen during 5 hr. at 75°, after which absorption becomes much slower.[1] About 41% of the absorbed oxygen was present in sulphoxide groups at this stage, and formation of water was evident from the opacity of the reaction mixture. Chromatography of the dried solution on silica gel separated the original sulphide and dimethyl disulphide from oxygenated products, but did not appreciably resolve the latter. Distillation of the total reaction mixture at 14 mm. gave, without noticeable decomposition, a volatile fraction (unchanged sulphide, dimethyl disulphide, water, but-2-enal, and a small amount of a saturated carbonyl compound), together with an involatile residue (A). Analyses of the latter indicated an approximate formula $C_5H_{10}OS$, *i.e.*, but-2-enyl methyl sulphoxide, but the sulphoxide content was only about half that required for this identity. The complex infrared spectrum indicated the presence of hydroxyl and vinylic C–S groups as well as sulphoxide. Partition between light petroleum, water, and methanol gave an essentially oxygen-free and sulphoxide-free product (B) in the petroleum layer, and an extract in the water–methanol layer which, after isolation and counter-current distribution between ether and water, furnished pure but-2-enyl methyl sulphoxide (in the water) and a hydroxylic compound (C) (in the ether).

After further purification, the product (B) gave correct analyses for $C_6H_{12}S_2$, and was first believed to be the thioacetal $CHMe{:}CH{\cdot}CH(SMe)_2$. However, its spectroscopic properties were incompatible with this structure, and pointed to its being the methylthio-substituted vinyl sulphide, $MeS{\cdot}CHMe{\cdot}CH{:}CH{\cdot}SMe$. Attempts to synthesize the thioacetal from but-2-enal and methanethiol by the procedure used by Hall and Moore[4] for the diethyl analogue gave a product virtually identical with (B) in respect of analysis, refractive index, and spectroscopic properties. Thus either allylic thioacetals, under the reaction conditions, spontaneously undergo an anionotropic-type displacement of a methylthio-group (the driving force being development of vinylic sulphide conjugation), or attack of a thiol on the hemithioacetal precursor $CHMe{:}CH{\cdot}CH(OH){\cdot}SMe$ proceeds by an "abnormal" (S_N2') substitution[5] rather than at the thio-substituted saturated carbon atom (this type of reaction being favoured in systems where the substituent is a neutral molecule[6]).

The nature of the unstable product (C) has not been conclusively established but it is almost certainly the hemithioacetal. Attempts to isolate it gave but-2-enal whose 2 : 4-dinitrophenylhydrazone was obtained in good yield from the involatile residue (A) after removing free aldehyde at 10^{-5} mm. and then adding Brady's reagent in the cold. Owing to thermal decomposition of the hemithioacetal more crotonaldehyde and dimethyl disulphide were formed on distillation under atmospheric pressure at 140° (bath-temp.) than under 14 mm. at 50° (bath-temp.). The ready breakdown of other hemithioacetals into aldehyde and thiol on heating has been reported[7,8,9] and has been confirmed for $CH_2Me{\cdot}CH_2{\cdot}CH(OH){\cdot}SMe$, which was synthesized and found to decompose slowly into butanal, methanethiol, water, and more complex products even at room temperature.

Quantitative Estimation of the Oxidation Products.—The following product composition was determined at an oxygen uptake of 1·56% by weight, 86% of the absorbed oxygen being accounted for :

	H_2O	$CHMe{:}CH{\cdot}CHO$	$CHMe{:}CH{\cdot}CH_2{\cdot}SOMe$	$CHMe{:}CH{\cdot}CH(OH){\cdot}SMe$
Proportion of oxygen absorbed (wt. %) ...	16	17	41	12

Dimethyl disulphide and 1 : 3-dimethylthiobut-1-ene were formed to the extent of 0·23 and 0·26 mole per mole of oxygen absorbed.

Course of the Reaction.—Earlier work shows that autoxidation of allylic sulphides is a complex free-radical chain reaction initiated by abstraction of a hydrogen atom from the

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[4] Hall and Moore, *J.*, 1949, 2723.
[5] Hughes, *Trans. Faraday Soc.*, 1938, **34**, 185.
[6] Young, Webb, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1076.
[7] Schubert, *J. Biol. Chem.*, 1935, **111**, 671; 1936, **114**, 341.
[8] Kipnis and Ornfelt, *J. Amer. Chem. Soc.*, 1952, **74**, 1952.
[9] Levi, *Gazzetta*, 1932, **62**, 775.

methylene group activated by both the double bond and the thio-substituent.[1] The resulting radical then combines with oxygen to give a highly reactive peroxide, which appears to oxidize the parent sulphide to sulphoxide and, in reduced form, to undergo scission at the C–S bond to oxygenated olefins and disulphides.[1,2] Information about the secondary reactions has recently come from studies of the reaction of hydroperoxides with organic sulphides.[10–12]

Unlike saturated sulphides, which react with hydroperoxides under various conditions strictly according to reaction (1),

$$R_2S + R'O_2H \longrightarrow R_2SO + R'OH \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

allylic sulphides do so only in hydroxylic solvents or other special circumstances.[11,12] In organic solvents the yield of allylic sulphoxide is generally much less, and other products, such as water and disulphide, are then formed. The secondary reactions involve, as reactants, sulphoxide, hydroperoxide, and sulphide,[12] to extents which vary for different sulphides; they lead to disulphide, water, and unknown products. The yields of sulphoxide obtained on autoxidation and on reaction with hydroperoxide from a series of compounds run parallel (Table 1). It is therefore concluded that similar secondary reactions occur in both cases. It would then be expected (*a*) that the yields of sulphoxide should approach the theoretical in the early stage of oxidation and fall later as the sulphoxide first produced decomposes in secondary reactions, and (*b*) that addition of sulphoxide initially should result in the decrease in yield occurring at an earlier stage of oxygen absorption. Both these features have been observed (Figs. 1 and 2).

TABLE 1.

	Yield of sulphoxide (%)	
Sulphide	On reaction with Bu^tO_2H in C_6H_6 at 50° *	On autoxidation at 75° †
$CHMe{:}CH{\cdot}CHMe{\cdot}S{\cdot}Bu^n$	2	5
$CHMe{:}CH{\cdot}CHMe{\cdot}S{\cdot}Me$	4	5·5
$CH_2{:}CH{\cdot}CHMe{\cdot}S{\cdot}Bu^n$	15	6·5
cyclo-$C_6H_9{\cdot}S{\cdot}Me$	21	13
$CHMe{:}CH{\cdot}CH_2{\cdot}S{\cdot}Me$	28	22
$CHPh{:}CH{\cdot}CH_2{\cdot}S{\cdot}Bu^n$	47	24

* In respect of both oxygen atoms in the hydroperoxide, on complete reaction with excess of sulphide.

† After 24 hours, whereafter reactions are all auto-inhibited.

It is considered therefore that the overall autoxidation comprises three stages: (1) peroxidation of the sulphide by a free-radical chain reaction; (2) hydroperoxide–sulphide interaction to produce sulphoxide; and (3) decomposition of the primary products. Earlier reaction schemes [1] can thus be defined more precisely as follows (where R is vinyl):

Stage 1. $CH_2R{\cdot}SMe \longrightarrow CHR{\cdot}SMe$ Chain-initiation

$$\left.\begin{array}{r}{\cdot}CHR{\cdot}SMe + O_2 \longrightarrow {\cdot}O_2{\cdot}CHR{\cdot}SMe \\ {\cdot}O_2{\cdot}CHR{\cdot}SMe + CH_2R{\cdot}SMe \longrightarrow HO_2{\cdot}CHR{\cdot}SMe + {\cdot}CHR{\cdot}SMe\end{array}\right\}\ \text{Chain-propagation}$$

Stage 2. $HO_2{\cdot}CHR{\cdot}SMe + CH_2R{\cdot}SMe \longrightarrow HO{\cdot}CHR{\cdot}SMe + CH_2R{\cdot}SOMe$

Stage 3. $HO{\cdot}CHR{\cdot}SMe + CHR{\cdot}SOMe \longrightarrow Me_2S_2 + H_2O + \text{etc.}$ . . . . (3)

$$HO{\cdot}CHR{\cdot}SMe \longrightarrow R{\cdot}CHO + MeSH \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$HO{\cdot}CHR{\cdot}SMe + MeSH \longrightarrow MeS{\cdot}CHR'{\cdot}CH{:}CH{\cdot}SMe + H_2O \qquad . \; . \; . \; . \quad (5)$$

Since inhibition by substances such as quinol shows that the reaction chain of stage 1 is long,[1] chain-termination is insignificant in the present context. The reactions shown for stage (3), although not determined exactly, provide plausible routes to the final products. Reaction (3) is advanced in part by analogy with that for hydroperoxide, but the

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[10] Bateman and Hargrave, *Proc. Roy. Soc.*, 1954, *A*, **224**, 389, 399.

[11] Barnard, *J.*, 1956, 489.

[12] Hargrave, *Proc. Roy. Soc.*, 1956, *A*, **235**, 55.

hemithioacetal, rather than the hydroperoxide, is considered to be involved because (*a*) hydroperoxide groups react very readily in stage (2) and thus are found only in very small amounts in the product mixture at any time, and (*b*) heating either the total oxidation product or the involatile residue (A) (p. 3057) (which contains hemithioacetal but not hydroperoxide) causes decomposition of sulphoxide with the formation of disulphide and water.

On this reaction scheme, the final product composition will be determined by the extent to which the products of stage (2) participate in stage (3) and this is expressed by the extent to which less than 50% of the absorbed oxygen is found as sulphoxide. If for each 6 molecules of the hydroperoxide-sulphide and the sulphide which interact in stage 2, two molecules of the hemithioacetal engage in each of the reactions (4) and (5), and one in reaction (3), a product composition can be derived which agrees with experiment (Table 2). The significance of this agreement clearly depends on the wider validity of the derivation, and two other sulphides, distinctively different from but-2-enyl methyl sulphide in certain autoxidation characteristics, have therefore been examined.

FIG. 1. *Decrease in yield of sulphoxide during autoxidation of but-2-enyl methyl sulphide at* 75°.

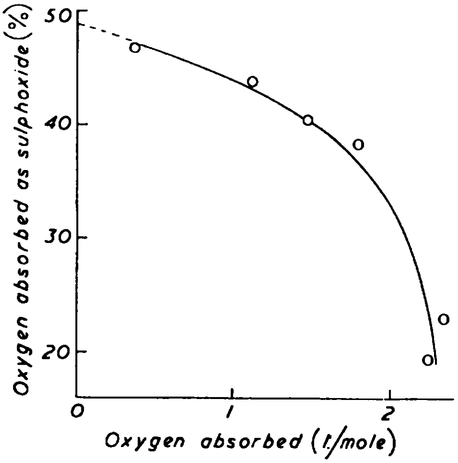
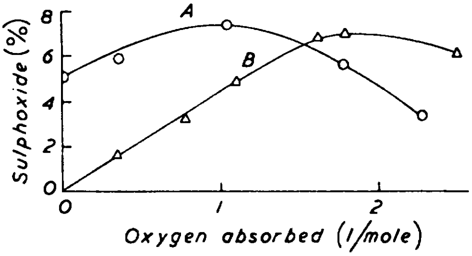


FIG. 2. *Effect of added sulphoxide on sulphoxide content of autoxidised but-2-enyl methyl sulphide.*



A, Sulphoxide added initially (5·1%).
B, No addition.

TABLE 2.

Product	Molar proportions	
	Found	Calc.
$\mathrm{CHMe{:}CH{\cdot}CH_2{\cdot}SO{\cdot}Me}$	1·0	1·0
$\mathrm{CHMe{:}CH{\cdot}CHO}$	0·4	0·4
$\mathrm{H_2O}$	0·39	0·6
$\mathrm{CHMe{\cdot}SMe{\cdot}CH{:}CH{\cdot}S{\cdot}Me}$	0·31	0·4
$\mathrm{CHMe{:}CH{\cdot}CH(OH){\cdot}S{\cdot}Me}$	0·29	0·2
$\mathrm{Me_2S_2}$	0·27	0·2

Methyl 1-methylbut-2-enyl sulphide is oxidized more readily than the but-2-enyl homologue (cf. the *n*-butyl homologues [2]) until the inhibitory process stops the reaction at an oxygen uptake of *ca.* 3·8% (at 75°). The yield of sulphoxide is much lower, only 10% of the oxygen being thus combined at an uptake of 1·6%, as compared with 41% in but-2-enyl methyl sulphide. This indicates the increased importance of stage 3 and greater instability of the sulphoxide, in conformity with the low sulphoxide yield in the corresponding sulphide–hydroperoxide reaction (Table 1). This is strikingly shown in the decrease in yield of sulphoxide as oxidation proceeds (Fig. 3), which is more marked than with but-2-enyl methyl sulphide yet shows the same feature of extrapolation to nearly the " theoretical " value (*i.e.* stage 3 absent) at zero uptake.

The products contain different ratios of sulphoxide : water : dimethyl disulphide as compared with the but-2-enyl system, *viz.*, 1·0 : 2·5 : 2·6 instead of 1·0 : 0·39 : 0·27. The ratios calculated as above for a sulphoxide yield of 10% and on the assumption of complete decomposition of the hemithioacetal (*i.e.*, for ***maximum*** yields of water and dimethyl disulphide) are 1 : 4·5 : 4·0, which again expresses the essential experimental results. The reversal in the relative yield of sulphoxide to the scission products is thus explained semi-quantitatively.

The influence of sulphoxide decomposition can be directly examined in the autoxidation of saturated acyclic sulphide since the derived sulphoxide does not undergo secondary decomposition in the sulphide–hydroperoxide reaction,[11] *i.e.*, stage 3 is absent. Experiment confirms this.

Although *n*-butyl methyl sulphide does not autoxidize by itself, it does so readily in the presence of azo*iso*butyronitrile.[1] In marked contrast to the unsaturated sulphides, the yield of sulphoxide, 31%, is constant throughout the reaction (Fig. 3) and is not influenced by the addition of *n*-butyl methyl sulphoxide initially. The products (with 88% of the absorbed oxygen accounted for) contain much water, but, again in contrast to the methyl 1-methylbut-2-enyl sulphide system, little dimethyl disulphide.* This confirms the kinetic characteristics in indicating that *n*-butyl methyl sulphoxide remains stable in the autoxidizing sulphide, and that the hemithioacetal, which is not found as a product, decomposes to form water by reactions other than (3) and (5). If reactions (6) and (7) are substituted for (3) and (5) in stage 3 :

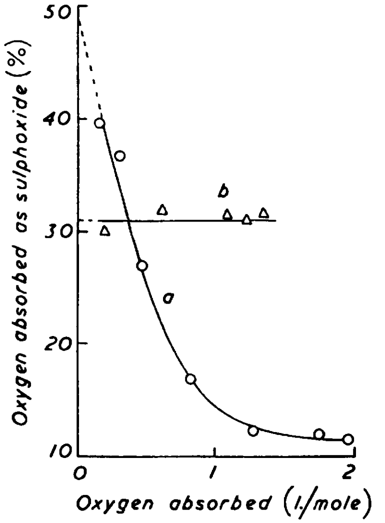


FIG. 3. *Variation in yield of sulphoxide during autoxidation of* (*a*) 1-*methylbut*-2-*enyl methyl sulphide at* 45° *and* (*b*) n-*butyl methyl sulphide at* 75°.

$$\tfrac{1}{2}\mathrm{HO_2{\cdot}CHR{\cdot}SMe} + \tfrac{1}{2}\mathrm{HO{\cdot}CHR{\cdot}SMe} \longrightarrow \mathrm{H_2O} + \text{etc.} \qquad (6)$$

$$\tfrac{1}{2}\mathrm{HO{\cdot}CHR{\cdot}SMe} \longrightarrow \tfrac{1}{2}\mathrm{R{\cdot}CHO} + \tfrac{1}{2}\mathrm{MeSH} \qquad (4)$$

$$\tfrac{1}{2}\mathrm{MeSH} + \tfrac{1}{8}\mathrm{O_2} \longrightarrow \tfrac{1}{4}\mathrm{Me_2S_2} + \tfrac{1}{4}\mathrm{H_2O} \qquad (7)$$

then both the yield of sulphoxide (calc. 31%) and the relative proportions of the products agree with the experimental values (Table 3). The formation of *n*-butyl methyl disulphide indicates that the initiation reaction involves the methyl group to a minor extent, in agreement with the previous conclusions on the relative reactivity of methyl and methylene groups.

To summarize, there is strong evidence that stages 1 and 2 represent the primary

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* Control experiments with unsaturated sulphides shows that the presence of the catalyst does not appreciably affect the products.

TABLE 3.

	Molar proportions			Molar proportions	
Product	Found	Calc.	Product	Found	Calc.
$Bu^n\cdot SO\cdot Me$	1·0	1·0	Me_2S_2	0·3	0·25
$Pr^n\cdot CHO$	0·6	0·5	$Bu^n_2S_2$	0·1	0·0
H_2O	1·2	1·25			

autoxidation of sulphides of the type now considered, which is actually encountered in allylic sulphides only at very small extents of reaction. The subsequent decomposition of the relatively labile products varies in extent and kind from one system to another, but in a way which can be given a general explanation.

EXPERIMENTAL

The sulphides were those described in Part III.[1]

Oxidation Procedure.—Small-scale experiments for kinetic and certain analytical measurements were carried out in the apparatus referred to previously (Fig. 1 in Part III). Oxidations on a larger scale (*ca.* 200 g. of sulphide) were carried out in a flask attached to a gas-burette containing oxygen over silicone oil,[1] the pressure being kept approximately constant by manual control.

Oxidation of But-2-enyl Methyl Sulphide.—Of procedures examined, the following gave the most effective separation of the products. The oxidized sulphide (82·6 g. containing 1·29 g. of oxygen) was heated at 60° (bath)/14 mm. and the volatile materials (74·4 g.) were collected in a trap at −80°. After drying (Na_2SO_4), this distillate gave analyses for unchanged sulphide (Found: C, 59·0; H, 9·8; S, 31·5. Calc. for $C_5H_{10}S$: C, 58·8; H, 9·85; S, 31·3%). However, infrared absorption at 1700, 1720, and 1750 $cm.^{-1}$ showed the presence of carbonyl groups, and addition of 2 : 4-dinitrophenylhydrazine hydrochloride in ethanol precipitated but-2-enal 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 191° (Found: C, 47·8; H, 4·2; N, 22·9. Calc. for $C_{10}H_{10}O_4N_4$: C, 48·0; H, 4·0; N, 22·5%). Treatment with lithium aluminium hydride in dry ether liberated methanethiol, which was absorbed in alcoholic sodium hydroxide and identified as methyl 2 : 4-dinitrophenyl sulphide, m. p. and mixed m. p. 126·5—127° (Found: C, 39·2; H, 2·2; N, 13·3; S, 14·9. Calc. for $C_7H_6O_4N_2S$: C, 39·3; H, 2·8; N, 13·2; S, 15·0%).

The involatile residue (A) (7·7 g.) had n_D^{20} 1·5080 (Found: C, 50·6; H, 8·3; S, 28·2; SO content, 51%), and its infrared and ultraviolet spectra indicated the presence of hydroxyl and vinylic sulphide groups in addition to sulphoxide. The constituents were separated by solvent distribution as follows:

(i) The sample (27·5 g.) was shaken with a mixture of light petroleum (b. p. <40°; 60 ml.), water (30 ml.), and methanol (30 ml.). The aqueous layer was extracted twice with light petroleum (60 ml.) and the combined petroleum extracts were first washed with aqueous methanol (50 : 50; 2 × 60 ml.) and the solvent was then removed by distillation. The residue (B) (6·2 g.; n_D^{20} 1·5433) contained only a little sulphoxide (Found: C, 49·3; H, 7·9; S, 38·8; SO content, 2·0%), which was further removed by chromatography. A portion of (B) (2·7 g.) in light petroleum (b. p. <40°; 150 ml.) was passed through silica gel (200 mesh; 30 × 1·8 cm.) followed by light petroleum (1) (200 ml.), (2) (200 ml.), (3) light petroleum–carbon tetrachloride (50 : 50; 200 ml.), (4) carbon tetrachloride (200 ml.), (5) ether (200 ml.), (6) ether (200 ml.), (7) chloroform (200 ml.), and (8) methanol (200 ml.). Fractions (2)—(4) and (6)—(8) gave only traces of extract. Fraction (1) gave a product (1·6 g.), n_D^{20} 1·5460 (Found: C, 49·1; H, 8·2; S, 42·7%; *M*, 150. $C_6H_{12}S_2$ requires C, 48·8; H, 8·1; S, 43·2%; *M*, 148), identified as 1 : 3-*dimethylthiobut*-1-*ene* (see below). Fraction (5) gave a product (0·6 g.), n_D^{20} 1·5390 (Found: C, 49·5; H, 7·9; S, 28·1; SO content, 6·0%), which was a complex mixture of hydroxyl, carbonyl, and sulphoxide compounds.

The combined methanol–water layers were saturated with sodium chloride and extracted with chloroform (5 × 100 ml.). Evaporation of the chloroform from the combined extracts gave a sulphoxide-rich product (18·2 g.), n_D^{20} 1·5056 (Found: C, 48·4; H, 8·0; S, 27·1; SO content, 74·7%), of which 6·5 g. were subjected to countercurrent distribution between ether and water in a 20-cell apparatus. The ether extract gave a product very similar to fraction (5) above. The water extracts were saturated with salt and extracted with chloroform, which yielded but-2-enyl methyl sulphoxide (4·7 g.), b. p. 54—55°/0·02 mm., n_D^{20} 1·5038 (Found: C, 50·5; H, 8·5; S, 26·8; SO content, 99·4. Calc. for $C_5H_{10}OS$: C, 50·8; H, 8·5; S, 27·1%).

(ii) Fraction A (10 g.) was shaken with light petroleum (10 ml.) and water (10 ml.), the aqueous layer was separated, extracted twice with light petroleum (10 ml.), and the combined light petroleum extracts were then washed with water (2 × 10 ml.). The petroleum extracts gave a product (2·65 g.), practically identical with (B) above. The combined aqueous extracts were continuously extracted with methylene chloride for two days, the latter extract yielding a sulphoxide-rich product similar to that above from the methanol–water extracts in (i) (5·3 g.), n_D^{20} 1·5042 (Found: C, 50·5; H, 8·3; S, 26·3; SO content, 78·1%). The extracted water layer was evaporated down under reduced pressure, only a trace of residue being obtained. Spectroscopic examination of all the solvents used and recovered in those extracts showed only the presence of but-2-enal, in addition to the vinyl sulphide and but-2-enyl methyl sulphoxide actually isolated.

Synthesis of 1 : 3-*Dimethylthiobut*-1-*ene*.—Methanethiol (15 g.) was added to but-2-enal (7 g.) in carbon tetrachloride (20 ml.) containing dry hydrogen chloride (0·05 g.) and cooled to 0°. After being kept at room temperature overnight, the solvent and excess of thiol were evaporated, and the residue was separated by distillation into (i) mainly 3-methylthiobutanal, b. p. 80—92°/14 mm., n_D^{20} 1·5078 (2 : 4-dinitrophenylhydrazone, m. p. 85—86°), and (ii) 1 : 3-dimethylthiobut-1-ene, b. p. 92—93°/14 mm. (6 g.), n_D^{20} 1·5465 (Found: C, 48·6; H, 8·0; S, 43·4. $C_6H_{12}S_2$ requires C, 48·7; H, 8·1; S, 43·2%).

Synthesis of 1-*Methylthio- and* 1-*Ethylthio-oct*-1-*ene*.—Solutions of the respective thiols in oct-1-yne were sealed in glass tubes under a vacuum and irradiated for 5 hr. at a distance of 6″ from a Hanovia 500 w mercury lamp. The addition products isolated by distillation were characterized as follows: 1-*methylthio-oct*-1-*ene*, b. p. 88—89°/14 mm., n_D^{20} 1·4780 (Found: C, 68·1; H, 11·3; S, 19·9. $C_9H_{18}S$ requires C, 68·3; H, 11·4; S, 20·3%); 1-*ethylthio-oct*-1-*ene*, b. p. 46°/0·01 mm., n_D^{20} 1·4755 (Found: C, 69·7; H, 11·8; S, 18·9. $C_{10}H_{20}S$ requires C, 69·8; H, 11·6; S, 18·6%).

Spectra of the Vinyl Sulphides.—The ultraviolet absorption bands given by simple vinyl sulphides, by a synthetic sample of 1 : 3-dimethylthiobut-1-ene, and by a sample isolated from the oxidation of but-2-enyl methyl sulphide (in ethanol) were:

	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
$\mathrm{MeS{\cdot}CH{:}CH{\cdot}C_6H_{13}}$	2280	6057	2450	3375
$\mathrm{EtS{\cdot}CH{:}CH{\cdot}C_6H_{13}}$	2300	5780	2450	4080
$\mathrm{MeS{\cdot}CHMe{\cdot}CH{:}CH{\cdot}SMe}$, synth.	2300	8790	2480	6970
,, from oxidn. product	2300	8720	2480	7040

The infrared spectra of the last two samples were identical and were characterized by strong absorption at 1597 cm.$^{-1}$ due to the $\mathrm{C{:}C{\cdot}S{\cdot}}$ grouping.

Quantitative Estimation of Oxidation Products.—Sulphoxide was estimated directly in the reaction mixture by reduction with titanous chloride.[13]

Water was estimated in the reaction mixture, essentially by the procedure described by Bateman and Shipley.[2]

Dimethyl disulphide was estimated in the volatile fraction by reduction with lithium aluminium hydride [2] and polarographically in the total oxidation mixture.[2]

Crotonaldehyde was estimated, in the reaction mixture and the volatile fraction, (*a*) spectroscopically (comparison of intensity of infrared absorption at 1700 cm.$^{-1}$ due to conjugated carbonyl groups) and (*b*) polarographically [comparison of the wave given in 85% acetone-free methanol–15% water containing an acid buffer (HCl and NaOAc) with that given by an authentic sample of crotonaldehyde under the same conditions].

1 : 3-Dimethylthiobut-1-ene was estimated spectroscopically on fraction (A) (p. 3061) by measurement of the intensity of absorption at 2300 Å, allowance being made for absorption by the admixed sulphoxide and butenal.

Hydroxyl groups, attributed to 1-methylthiobut-2-en-1-ol, was estimated in fraction (A) by reaction with phthalic anhydride in pyridine.[14] Blank estimations were made with synthetic mixtures of butan-1-ol, but-2-enal, and but-2-enyl methyl sulphoxide, which showed that the last two compounds did not interfere with analysis of the first.

Attempted Syntheses of 1-*Methylthiobut*-2-*en*-1-*ol*.—(i) Methanethiol (1 g.) in ethanol (3 ml.)

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[13] Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 536.

[14] Eloving and Warshowsky, *Analyt. Chem.*, 1947, **19**, 1006.

was added slowly to but-2-enal (3 g.) in ethanol (3 ml.) and the mixture left in the dark at room temperature overnight.[7] Evaporation at 40°/14 mm. gave a residue (0·7 g.), b. p. 20°/0·002 mm., n_D^{20} 1·4948 (Found: C, 52·6; H, 8·9; S, 28·1. Calc. for $C_5H_{10}OS$: C, 50·8; H, 8·5; S, 27·1%) (OH infrared absorption bands absent), which appeared to be a mixture of β-methylthiobutyraldehyde and 4-ethoxy-4-methylthiobut-2-ene. (ii) Methanethiol (1·5 g.) in ether (7 ml.) was added to but-2-enal (4·7 g.) in ether (5 ml.) and the mixture kept at room temperature for 5 days. Evaporation at reduced pressure left a product (2·8 g.), n_D^{20} 1·4963. No hydroxyl groups were detected by infrared spectroscopy, and the product was largely β-methylthiobutyraldehyde (2 : 4-dinitrophenylhydrazone, m. p. 85—86°).

Synthesis of 1-*Methylthiobutan*-1-*ol*.—Methanethiol (6 g.) in ether (45 ml.) was added in 1 hr. to butyraldehyde (54 g.), cooled in ice and rapidly stirred, and the mixture kept at room temperature for 4 days. Evaporation at 20°/14 mm. and then at 0·005 mm. into a trap at −80° gave in the trap mainly the desired hemithioacetal (with a little aldehyde), n_D^{20} 1·4646 (Found: C, 52·7; H, 10·2; S, 23·6%; *M*, 119. Calc. for $C_5H_{12}OS$: C, 50·0; H, 10·0; S, 27·3%; *M*, 120). Its infrared spectrum had a strong OH band at 1725 cm.$^{-1}$. On storage under nitrogen at room temperature, it slowly decomposed with liberation of water.

Evidence for Presence of 1-*Methylthiobut*-2-*en*-1-*ol in Oxidation Products*.—(i) But-2-enyl methyl sulphoxide did not react with the hydrazine hydrochloride in ethanol at room temperature. (ii) The total oxidation product under the same conditions immediately gave a 2 : 4-dinitrophenylhydrazone, m. p. 177—185° (Found: C, 47·0; H, 4·0; N, 21·8; S, 1·0. Calc. for $C_{10}H_{10}O_4N_4$: C, 48·0; H, 4·0; N, 22·5%), $\lambda_{max.}$ 3740 Å ($E_{1\,cm.}^{1\%}$ 1124 in EtOH), which on one crystallization from ethanol–benzene had m. p. and mixed m. p. (with but-2-enal 2 : 4-dinitrophenylhydrazone) 191°, $\lambda_{max.}$ 3730 Å ($E_{1\,cm.}^{1\%}$ 1075 in EtOH). (iii) The small amount of but-2-enal present in fraction A (p. 3061) (*ca.* 3%) was removed at 10^{-5} mm. at room temperature: its characteristic smell and infrared spectrum were then no longer detected. Addition of the hydrazine, however, gave a derivative, m. p. 165—175° (Found: C, 47·2; H, 4·1; N, 22·1; S, 0·9%), $\lambda_{max.}$ 3740 Å ($E_{1\,cm.}^{1\%}$ 1044 in EtOH), which after one crystallization from ethanol–benzene had m. p. 191° alone or mixed m. p. with the but-2-enal derivative.

Fraction (A) thus contains a hydroxylic component readily giving but-2-enal on treatment with ketonic reagents. The hemithioacetal satisfies this requirement and the elementary analysis (when allowance is made for the other constituents present in known amount). The comparative stability of the hemithioacetal in the total oxidation product and in fraction (A) contrasts with its dissociation on attempted isolation from solvents (p. 3062). This may be due to complex formation with the sulphoxide in the first two systems, which evidently decomposes under more vigorous conditions than encountered in the isolation of (A), since heating this fraction at 75° for 24 hr. reduces the sulphoxide content from 51 to 7%, and water and disulphide are produced.

Experiments with Methyl 1-*Methylbut*-2-*enyl Sulphide*.—The oxidation of this sulphide was followed quantitatively in the small-scale apparatus (p. 3061). Estimations of the products were carried out by the procedures indicated above, their validity having been established by blank determinations. At an oxygen uptake of 1·6%, the following results were obtained:

	Wt. (%)	Mole per mole of O_2 absorbed
Sulphoxide	1·32	0·20
Water	0·45	0·50
Dimethyl disulphide	2·44	0·52

Sulphoxide yields measured at other extents of reaction are plotted in Fig. 3.

n-*Butyl Methyl Sulphide*.—(*a*) The sulphide (100 g.) containing αα′-azo*iso*butyronitrile (1 g.) was shaken at 75° with oxygen at atmospheric pressure. After 10·5 hr. 1·75 g. of oxygen had been absorbed, and absorption was very slow. Distillation at 60°/14 mm. gave a volatile fraction, consisting of unchanged sulphide admixed with water, butyraldehyde, and dimethyl disulphide (Found, after drying over $MgSO_4$: C, 57·9; H, 11·6; S, 30·6%), and a residue (6·8 g.) (Found: C, 48·8; H, 9·2; N, 2·9; S, 23·9; SO content, 54·5%).

Shaking the volatile fraction (60 g.) with freshly prepared saturated aqueous sodium hydrogen sulphite for 2 hr., and adding Brady's reagent to the aqueous layer in the cold, gave butyraldehyde 2 : 4-dinitrophenylhydrazone (2·05 g.), m. p. and mixed m. p. 122°. After being dried, the organic layer contained no hydroxyl or carbonyl groups detectable by infrared spectroscopy.

Dimethyl disulphide was detected in the volatile fraction by the liberation of methanethiol (identified as 2 : 4-dinitrophenyl methyl sulphide, m. p. 126·5°) on treatment with lithium aluminium hydride.

The involatile fraction of the oxidation product (30 g.) was dissolved in aqueous methanol (1 : 1; 60 ml.) and extracted with light petroleum (b. p. <40°; 3 × 60 ml.). The combined petroleum extracts were extracted twice with aqueous methanol, dried (Na_2SO_4), and evaporated. The residue (5·25 g.) had n_D^{20} 1·5040 and contained little sulphoxide (Found : C, 46·8; H, 8·8; N, 0·8; S, 40·6; SO content 2·1%; *M*, 142). Adsorption of 1 g. of this residue on alumina and elution with light petroleum gave a product (0·8 g.), n_D^{20} 1·5124, containing *n*-butyl methyl disulphide (74%) and di-*n*-butyl disulphide (26%) (Found : C, 46·8; H, 8·9; S, 44·4. Calc. for the mixture : C, 46·6; H, 9·1; S, 44·2%). Attempted fractionation showed the absence of dimethyl disulphide, and reduction with lithium aluminium hydride gave methanethiol (identified as 2 : 4-dinitrophenyl methyl sulphide) and butane-1-thiol [2 : 4-dinitrophenyl derivative, m. p. and mixed m. p. 65° (Found : C, 47·0; H, 4·7; N, 11·2. Calc. for $C_{10}H_{12}O_4N_2S$: C, 46·9; H, 4·7; N, 10·9%)]. The absence of mercaptals in the eluted product was shown by the non-formation of carbonyl compounds with refluxing aqueous mercuric chloride (30 min.).

The combined aqueous-methanol extracts yielded a product (22·2 g.) (Found : SO content, 75%), which on purification by counter-current distribution between ether and 2N-hydrochloric acid gave (from the acid layer) n-*butyl methyl sulphoxide* (14 g.), n_D^{20} 1·4694 (Found : SO content, 99%), characterized by oxidation[15] to *n*-butyl methyl sulphone, m. p. and mixed m. p. 28·5—29·5°. The sulphoxide was also identical with a specimen (prepared from the sulphide[10]), b. p. 51·5°/0·01 mm., n_D^{20} 1·4695 (Found : C, 50·1; H, 10·0; S, 26·3; SO content 99·0. $C_5H_{12}OS$ requires C, 50·0; H, 10·0; S, 26·7%).

(*b*) Sulphoxide and water were estimated by the procedures already described (p. 3062), blank determination having established their validity for the *n*-butyl methyl sulphide system. Results for the sulphoxide are shown in Fig. 3, and for water were :

O_2 absorbed (wt. %)	0·90	1·58	1·93
O_2 absorbed found as water (%)	37·0	37·0	37·4

Butyraldehyde was estimated (*a*) spectroscopically (by comparisons of the intensity of infrared absorption by the saturated carbonyl group at 1725 cm.⁻¹) and (*b*) gravimetrically (by quantitative extraction with sodium hydrogen sulphite and precipitation of the 2 : 4-dinitrophenylhydrazone as described above). The results were :

Method	(*a*)	(*b*)	(*b*)
O_2 (wt. %)	1·0	1·0	1·75
O_2 adsorbed found as aldehyde (%)	23·8	21·2	19·0

Dimethyl disulphide was estimated by reducing the total oxidation product with lithium aluminium hydride and measuring the methanethiol liberated (p. 3062). The extent of formation of di-*n*-butyl disulphide was calculated from the weight and composition of the mixed disulphide fraction (above). For present purposes, *n*-butyl methyl disulphide may be considered as derived by disproportionation of the symmetrical disulphides. At 1·75 wt. % of oxygen absorbed, the total oxidation product contained 1·0 wt. % of dimethyl disulphide and 0·69 wt. % of di-*n*-butyl disulphide, *i.e.*, 0·19 and 0·07 mole per mole of oxygen absorbed respectively.

Oxidation of n-*Butyl Methyl Sulphide in the Presence of the Sulphoxide.*—The sulphide (10·15 g.), containing *n*-butyl methyl sulphoxide (0·4270 g.) and αα′-azo*iso*butyronitrile (0·10 g.), was shaken in oxygen at 75° until 1·44 wt. % had been absorbed. The sulphoxide content was then 7·3%; the calculated value on the basis that the added sulphoxide behaves as a neutral diluent having no influence on the oxidation is 7·35%.

We are indebted to Mr. M. E. Cain for experimental assistance. This work forms part of a programme of research undertaken by the Board of the British Rubber Producers' Research Association.

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[*Received, February* 14*th*, 1956.]

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[15] Cunneen, *J.*, 1947, 39.