100. *Oxidation of Organic Sulphides. Part V.* The Products of the Reaction of Organic Hydroperoxides with Alk-2-enyl Sulphides.*

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The yields of sulphoxides from the reaction of allylically unsaturated sulphides with several organic hydroperoxides have been found to be always less than the theoretical. The dependence of the yields upon sulphide and hydroperoxide structure, the solvent used, and the reaction conditions is discussed. The non-sulphoxidic products from the reaction of 1-methylbut-1-enyl *n*-butyl sulphide with *tert.*-butyl hydroperoxide in benzene appear to arise from C–S bond cleavage and consist of di-*n*-butyl disulphide and a complex mixture of oxygenated, sulphur-free substances, including alcohols, ethers, peroxides, water, and some polymeric material. Similar products are given by other sulphides.

The preliminary step in the ready autoxidation of unsaturated organic sulphides is considered to be formation of a hydroperoxide *via* a peroxy-radical, followed by intermolecular reaction of the hydroperoxide with a sulphide group.[1]

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* Part IV, Bateman and Shipley, *J.*, 1955, 1996.

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

It is of obvious importance to examine analogues of the latter reaction removed from the complexities of the autoxidising system, and this has been done in the case of saturated sulphides by Bateman and Hargrave.[2] In both polar and non-polar solvents oxygen transfer occurred, *via* a cyclic transition complex, to give quantitative yields of sulphoxides over a wide range of experimental conditions according to the stoicheiometric equation :

$$\mathrm{RO{\cdot}OH + R'SR'' = ROH + R'{\cdot}SO{\cdot}R''} \qquad (1)$$

That this equation holds for a wide variety of hydroperoxide structures is demonstrated by the use made of the reaction to estimate hydroperoxide yields from autoxidised olefins,[3] the values obtained being in close agreement with those given by a standard procedure.[4]

The autoxidation of sulphides is generally restricted to unsaturated structures, and the present work is therefore concerned with a preliminary survey of the reaction of hydroperoxides with allylic, acyclic sulphides, mainly with a view to examining the validity of equation (1) with respect to yields of sulphoxide.

The sulphoxide yields quoted below are the mean values of, at the least, duplicate experiments and are given as the percentage of the theoretical value based on equation (1). The reproducibility was, unless otherwise stated, excellent (generally within ±1%).

TABLE 1. *Sulphoxide yields in methanol as solvent after* 100 *hours at* 50° ± 0·1° *with* $\mathrm{Bu^tO_2H}$.

	Yield (%)		Yield (%)
$\mathrm{Bu^n}$ 1-methylprop-2-enyl	98·8	Allyl phenyl	99·4
$\mathrm{Bu^n}$ 2-methylprop-2-enyl	100·6	$\mathrm{Bu^n}$ 1-methylbut-2-enyl	11—96
But-2-enyl $\mathrm{Bu^n}$	100·0	$\mathrm{Bu^n}$ 1-methylbut-2-enyl *	99·6
Diallyl	99·0		

* With *cyclo*hexenyl hydroperoxide, not $\mathrm{Bu^nO_2H}$.

A stoicheiometric yield of sulphoxide was obtained from the reaction with *tert.*-butyl hydroperoxide in methanol (see Table 1) with all the sulphides used except *n*-butyl 1-methylbut-2-enyl sulphide for which variations were wide and arbitrary. With *cyclo*hexenyl hydroperoxide the yield from this sulphide, and the other examples, was always stoicheiometric. This parallels the results in aprotic solvents illustrated below.

With *tert.*-butyl hydroperoxide in benzene the sulphoxide yield was in no case stoicheiometric (see Table 2), varying from 90% to 5% under the conditions chosen.

TABLE 2. *Yields from* tert.*-butyl hydroperoxide in benzene.*

Sulphide	Temp.	Reaction period (hr.)	Yield of sulphoxide (%)
Diallyl	55°	100	20
Allyl Ph	,,	,,	38
$\mathrm{Bu^n}$ cinnamyl	,,	,,	93
Dibenzyl	,,	,,	90
But-2-enyl $\mathrm{Bu^n}$	50	,,	55
$\mathrm{Bu^n}$ 2-methylprop-2-enyl	,,	,,	72
,, ,,	55	,,	58
,, ,,	50	200	71
$\mathrm{Bu^n}$ 1-methylprop-2-enyl	50	100	18
*cyclo*Hexenyl Me	55	,,	41
,, ,,	,,	200	41
$\mathrm{Bu^n}$ 1-methylbut-2-enyl	50	100	5
,, ,,	,,	,,	5 *
,, ,,	,,	190	8 †
1-Methylbut-2-enyl Ph	,,	100	8
1-Methylbut-2-enyl Me	,,	,,	9
$\mathrm{Bu^t}$ 1-methylbut-2-enyl	,,	,,	62

* Sealed *in vacuo*. † Sealed in oxygen.

The yields from *n*-butyl 2-methylprop-2-enyl, but-2-enyl, 1-methylprop-2-enyl and 1-methylbut-2-enyl sulphide are 72, 55, 18, and 5% respectively, this being the same order

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

[3] Hargrave and Morris, *Trans. Faraday Soc.*, in the press.

[4] Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 476.

as that of enhancement of α-methylenic hydrogen activity in an allyl group undergoing similar methyl substitution.[5] This suggests at first sight that in the transition from polar to non-polar solvent a free-radical reaction, involving at some stage the α-methylenic hydrogen, becomes impressed upon the normal oxidation mechanism. However the excellent reproducibility of the sulphoxide yields is not in accord with this hypothesis since the balance between a free-radical and a molecular reaction would be expected to be more sensitively poised. Moreover the effect of free-radical inhibitors on the course of such oxidations [6] is directly opposed to the occurrence of a free-radical chain mechanism.

Also in Table 2 it can be seen that for *n*-butyl 1-methylbut-2-enyl sulphides replacement of the *n*-butyl group by methyl or phenyl groups had little effect whereas a striking increase in the sulphoxide yield resulted when the *tert.*-butyl group was introduced. Similar inexplicable and anomalous effects of the *tert.*-butyl group on the autoxidation of sulphides have been noted previously.[1]

The results for *n*-butyl 2-methylprop-2-enyl sulphide at 50° and 55° show that the yield decreases with an increase of temperature. This effect has been more fully investigated over a wider range of temperature and sulphides and found to be quite general.[6]

TABLE 3. *Sulphoxide yields from the reaction of sulphides with hydroperoxides in benzene after* 100 *hours.*

Sulphide	Hydroperoxide	Temp.	Yield (%)
Bu^n 2-methylprop-2-enyl	*tert.*-Butyl	55°	58
,, ,,	Tetralyl	,,	63
,, ,,	*cyclo*Hexenyl	,,	71
Bu^n 1-methylprop-2-enyl	*tert.*-Butyl	50	18
,, ,,	Cumyl	,,	16
,, ,,	Tetralyl	,,	15
,, ,,	*cyclo*Hexyl	,,	18
,, ,,	*cyclo*Hexenyl	,,	88
Bu^n 1-methylbut-2-enyl	*tert.*-Butyl	,,	5
,, ,,	Cumyl	,,	14
,, ,,	Tetralyl	,,	13
,, ,,	*cyclo*Hexyl	,,	13
,, ,,	*cyclo*Hexenyl	,,	98
*cyclo*Hexenyl Me	*tert.*-Butyl	55	41
,,	Cumyl	,,	79
,,	Tetralyl	,,	74
,,	*cyclo*Hexyl	,,	60
,,	*cyclo*Hexenyl	,,	97

Table 3 shows that sulphoxide yields depend also on the hydroperoxide used, *tert.*-butyl hydroperoxide invariably giving amongst the lowest yields and *cyclo*hexenyl hydroperoxide the highest from any given sulphide. The difference in the kinetic behaviour of *tert.*-butyl and *cyclo*hexenyl hydroperoxides in their reactions with saturated sulphides in benzene has been ascribed by Bateman and Hargrave [2] largely to two reasons, the relatively large difference in acid strength, and the ability of *tert.*-butyl hydroperoxide alone to form a solvent complex. In the present instance acid strengths do not appear to be a dominating factor since, although *tert.*-butyl hydroperoxide is the weakest acid of the series, tetralyl and not *cyclo*hexenyl hydroperoxide is the strongest.[7] It might be argued that a solvent–hydroperoxide complex possessing a high oxidant activity, as postulated by Bateman and Hargrave,[2] is a necessary precursor of the non-sulphoxidic products. However the formation of a complex with benzene has been observed by infrared spectroscopic methods [7] for both *tert.*-butyl and *cyclo*hexenyl hydroperoxide and any difference in behaviour between these hydroperoxides in benzene must now be thought of, if attributed at all to solvent interaction, in terms of the reactivity of the complex. Steric considerations do not seem to be of importance.

The use of an excess of *tert.*-butyl hydroperoxide (Table 4) significantly increased the

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[5] Bolland, *Trans. Faraday Soc.*, 1950, **46**, 358.

[6] Hargrave, *Proc. Roy. Soc.*, in the press.

[7] Barnard, Hargrave, and Higgins, European Molecular Spectroscopy Group, Oxford, July, 1955, and forthcoming publication.

yield of sulphoxide and more hydroperoxide disappeared than could be accounted for by the sulphide originally present. This " loss " of hydroperoxide, which was approximately equal to the deficiency in the sulphoxide yield, was not due to sulphone formation since at most minute amounts of this product were detected. Moreover although diallyl sulphoxide, as a typical example, did react with *tert.*-butyl hydroperoxide in benzene to give products other than sulphone the rate of disappearance of either component was very slow under the standard reaction conditions.

TABLE 4 *Reaction of sulphides with a two-fold excess of* tert.*-butyl hydroperoxide in benzene at* 55°.

Sulphide	Reaction time (hr.)	Hydroperoxide used (% on sulphide)	Yield of sulphoxide (%)
*cyclo*Hexenyl Me	140	134	68
Bu^n 2-methylbut-2-enyl	100	114	90

Some of the observed facts can be accounted for by postulating that hydroperoxide may react with allylically unsaturated sulphides in two ways, one of which leads to sulphoxide and the other to a product, or products, which can further react rapidly with another equivalent of hydroperoxide.

$$R^1{\cdot}SO{\cdot}R^2 \xleftarrow[\text{Slow}]{(1)} R^1SR^2 \xrightarrow[\text{Slow}]{(2)} X \xrightarrow[\text{Fast}]{RO{\cdot}OH} Y$$

The balance between reactions (1) and (2) for individual sulphides and hydroperoxides wil determine the sulphoxide yield, each equivalent of sulphide participating in reaction (2) leading to loss of two equivalents of sulphoxide under normal conditions but to loss of only one when hydroperoxide is in excess. The temperature effect noted would be accounted for by the difference in activation energy between reactions (1) and (2), and the effect of solvent by the enhancement of reaction (1) in polar media (cf. Bateman and Hargrave [2]).

No further comment will be made here upon this or other possible explanations of the experimental findings since a more detailed mechanistic approach to the problem is to be presented later.[6]

As a knowledge of the composition of the non-sulphoxidic products should aid understanding of their origin, the reaction most favourable to their production, *i.e.*, that of *tert.*-butyl hydroperoxide with *n*-butyl 1-methylbut-2-enyl sulphide in benzene was more fully investigated.

The products from initially equivalent amounts (0·648 mole) of each reactant were separated by fractional distillation into water, *tert.*-butyl alcohol, a sulphur-free product A, di-*n*-butyl disulphide and a small amount of high-boiling material with high sulphur and oxygen contents. Minute amounts of hydrogen sulphide and volatile thiols were also detected. The oxygen, sulphur, and carbon balances were complete at this stage, so loss of volatile material was negligible. Only 68% of *tert.*-butyl alcohol was found, so *tert.*-butoxy-groups had been incorporated into the other products.

Product A was a complex mixture, not resolved by fractional distillation. It was divided into six arbitrary fractions of which fractions 4 and 6 (50% of the material) occurred at ill-defined boiling-point plateaux. All had a large oxygen content (13·6% in fraction 1 rising to a maximum of 20% in fraction 4) and infrared spectroscopy revealed hydroxyl (in fractions 1 and 2 only), carbonyl (minute amounts in all fractions) and C–O bands (strong in all fractions). Acetals and ketals were absent, for carbonyl compounds were not obtained on acid hydrolysis, and epoxide analyses, by Ross's method,[8] were negative. No fraction liberated iodine from potassium iodide in acetic acid, but all, more particularly fractions 3—6, liberated iodine when shaken with constant-boiling hydriodic acid at room temperature or, more rapidly, at 80°. Quantitative estimation of this peroxidic oxygen gave variable results owing apparently to addition of the free iodine to ethylenic double bonds, but an average value of 15% peroxidic oxygen was obtained for

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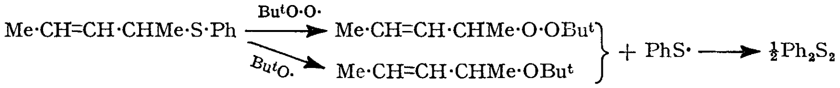
[8] Ross, *J.*, 1950, 2257.

fraction 4 and 6% for fraction 6. Determinations of total unsaturation by quantitative ozonolysis essentially according to Boer and Kooyman's method [9] agreed with the values found for *trans*-CH=CH– groups by infrared spectroscopy and, coupled with molecular-weight determinations, indicated that approximately one ethylenic double bond per molecule was present in fraction 4 and two per molecule in fraction 6. As most of the *n*-butyl groups originally present are accounted for as disulphide (cf. above), it can be tentatively assumed that some of the components in A are 1-methylbut-2-enol (in fractions 1 and 2), *tert.*-butyl 1-methylbut-2-enyl peroxide (in fraction 4), and bis-1-methylbut-2-enyl ether and peroxide (in fraction 6). These products indicate that one of the major reactions involves breaking of the bond between the allylic substituent and the sulphur atom.

In similar reactions with *tert.*-butyl hydroperoxide 1-methylbut-2-enyl phenyl sulphide gave mainly (*a*) a product very similar to product A and (*b*) diphenyl disulphide (91%). Water was again produced. However, *n*-butyl 1-methylallyl sulphide gave no water, and only a relatively small amount of the products was in the form of the " sulphur-free " and di-*n*-butyl disulphide fractions, the major product consisting of substances of molecular weight ranging from 200 to 600 and containing both sulphur and oxygen. The infrared spectra of these fractions were too diffuse to give useful information beyond presence of hydroxyl groups and loss of unsaturation. The product from allyl phenyl sulphide consisted entirely of similar high-boiling material. In the case of *n*-butyl 2-methylprop-2-enyl sulphide, sulphoxide was isolated in the yield indicated by analysis together with a small amount of di-*n*-butyl disulphide; no high-boiling material was formed.

It appears, therefore, that although carbon–sulphur bond scission occurs in most cases with the subsequent formation of disulphides, the inportance of this step varies very widely from sulphide to sulphide.

Some of the products from 1-methylbut-2-enyl phenyl sulphide and *tert.*-butyl hydroperoxide could have arisen by radical displacement reactions of *tert.*-butoxy- or *tert.*-butylperoxy-radicals with the sulphide, although, as has been already stated, it is not considered likely that free radicals play a part in the oxidation :



$$\mathrm{Me{\cdot}CH{=}CH{\cdot}CHMe{\cdot}S{\cdot}Ph}\left.\begin{array}{l}\xrightarrow{\mathrm{Bu^tO{\cdot}O{\cdot}}}\mathrm{Me{\cdot}CH{=}CH{\cdot}CHMe{\cdot}O{\cdot}OBu^t}\\ \xrightarrow[\mathrm{Bu^tO{\cdot}}]{}\mathrm{Me{\cdot}CH{=}CH{\cdot}CHMe{\cdot}OBu^t}\end{array}\right\}+\mathrm{PhS{\cdot}}\longrightarrow\tfrac{1}{2}\mathrm{Ph_2S_2}$$

The production of *tert.*-butylperoxy-radicals without presence of *tert.*-butyl hydroperoxide was not feasible but the possibility of reaction of the sulphide with *tert.*-butoxy-radicals was explored by thermally decomposing di-*tert.*-butyl peroxide in chlorobenzene in its presence. No fission products of the type found in the oxidation were detected but by a normal cross-linking process the sulphide gave a dimer, trimer, and some higher polymers. All the initial peroxide was accounted for as unchanged material, *tert.*-butanol, and acetone.

EXPERIMENTAL

Materials.—Solvents were purified and dried by standard procedures and fractionally distilled before use, the middle cut only being used.

*cyclo*Hexenyl and tetralyl hydroperoxides were prepared and purified as described by Barnard and Hargrave [4] and had purities of 95% and 99% respectively.

*cyclo*Hexyl hydroperoxide was prepared by the method of Walling and Buckler.[10] This and commercial samples of *tert.*-butyl and cumyl hydroperoxide were purified by successive regenerations from their sodium salts followed by fractional distillation and were obtained with purities of 97%, 100%, and 99% respectively.

The sulphides were synthesised by standard procedures described, together with the physical constants of most of the examples, by Bateman and Cunneen.[1] *n-Butyl 2-methylprop-2-enyl sulphide* had b. p. 65·8—66·2°/14 mm. (Found : C, 66·7; H, 11·1; S, 22·2. $C_8H_{16}S$ requires C, 66·7; H, 11·1; S, 22·2%). Allyl phenyl sulphide had b. p. 97·5—98°/14 mm., n_D^{20} 1·5761

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[9] Boer and Kooyman, *Analyt. Chim. Acta*, 1951, **5**, 550.

[10] Walling and Buckler, *J. Amer. Chem. Soc.*, 1953, **75**, 4372.

(Found: C, 72·1; H, 6·6; S, 21·3. Calc. for $C_9H_{10}S$: C, 72·0; H, 6·7; S, 21·2%). The sample of *cyclo*hexenyl methyl sulphide and samples of 1-methylbut-2-enyl sulphides were kindly provided by Drs. F. W. Shipley and J. I. Cunneen, respectively.

Method.—The following procedure was typical, deviations being specified in the text. The hydroperoxide (~0·45M) and the sulphide (~1·2M) dissolved in the appropriate solvent were sealed under purified nitrogen after thorough degassing *in vacuo*. To avoid possible catalysis the "Pyrex" glass vessels were cleaned with potassium permanganate in concentrated sulphuric acid, rinsed successively with water, ammonia solution, and distilled water, dried, and flamed. After being heated in a temperature-controlled water-bath for a period adequate for complete reaction the vessels were opened and the solvent was removed at low temperature *in vacuo*, the distillate being tested for active oxygen content (invariably negative). The residue was dissolved in "AnalaR" acetic acid and analysed for sulphoxide by Barnard and Hargrave's method.[11] When products were examined before the completion of the reaction, or when an excess of hydroperoxide was used, the acetic acid was replaced by *tert.*-butanol to avoid errors caused by acid-catalysed reactions of the hydroperoxide.

Reaction of n-*Butyl* 1-*Methylbut*-2-*enyl Sulphide with* tert.-*Butyl Hydroperoxide.*—A solution of the hydroperoxide (58·4 g.) and *n*-butyl 1-methylbut-2-enyl sulphide (102·4 g.) in benzene (500 ml.), degassed *in vacuo* and sealed under nitrogen, was kept at 50° ± 0·1° for 100 hr. The benzene, removed by fractional distillation, entrained water and *tert.*-butyl alcohol as the ternary and binary azeotropes, the former being dispersed as a fine suspension. Aliquot parts were analysed for (*a*) water by the Karl Fisher method[12] (Found: 3·01 g.) and (*b*) *tert.*-butyl alcohol by an infrared spectroscopic method involving the comparison of the strength of the absorption band at 3580 cm.$^{-1}$ with an appropriate calibration curve (Found: 32·5 g.). Water was first removed with anhydrous potassium carbonate, trial analyses indicating that this did not involve loss of *tert.*-butyl alcohol.

The residue left after removal of the solvent was fractionally distilled, to give product A (66·5 g.), b. p. 30—50°/11 mm., n_D^{20} 1·4280 (Found: C, 73·5; H, 11·3; S, 0·2%); product B (44·5 g.), b. p. 30—50°/0·01 mm., n_D^{20} 1·4910 (Found: C, 55·6; H, 9·85; S, 34·6%), and a higher-boiling fraction (b. p. 50—110°/0·01 mm., 10·6 g.) which was not further investigated.

Product A. This was further fractionated through a column of 12 theoretical plates. Six arbitrary fractions were collected over 27—53°/13 mm., of which the two largest were fraction 4 (12·2 g.), b. p. 44—46·5°/13 mm., n_D^{20} 1·4170 (Found: C, 68·7; H, 11·4%; *M*, 162), and fraction 6 (14·8 g.), b. p. 49—53°/13 mm., n_D^{20} 1·4290 (Found: C, 76·5; H, 11·5%; *M*, 152).

Determination of unsaturation. Fractions 4 and 6 were quantitatively ozonised in chloroform solution at −50° and absorbed 1·22 and 2·09 mols. of ozone respectively. Measurement of the strength of the 960 cm.$^{-1}$ band, with *trans*-but-2-enyl alcohol as standard, gave 0·9 and 1·84 *trans* −CH=CH− groups per molecule respectively.

Determination of peroxidic oxygen content. The sample (0·1 g.) and constant-boiling hydriodic acid (3 ml.), freshly distilled from red phosphorus in nitrogen, were sealed *in vacuo* and heated, with shaking, at 80° for 2 hr. After dilution with water liberated iodine was titrated with 0·1N-thiosulphate solution. Tar, which contained iodine, was usually formed. The iodine titre of blanks was always less then the equivalent of 0·05 ml. of 0·1N-solution. Fraction 4 gave peroxidic oxygen 13·2, 16·5, 15·4%. Fraction 6 gave peroxidic oxygen 5·4, 6·2, 6·6% (calc. for $C_9H_{18}O_2$: 20·2%).

Product B. A sample (7 g.) was fractionally eluted from activated alumina (20 × 1 cm.) with light petroleum (b. p. 40°; 100 ml.). The residue (6·5 g.) left after removal of the solvent had b. p. 44—45°/0·01 mm., n_D^{20} 1·4942 (Found: C, 53·8; H, 10·1; S, 35·7. Calc. for $C_8H_{18}S_2$: C, 53·95; H, 10·1; S, 35·95%), and an infrared spectrum indistinguishable from that of di-*n*-butyl disulphide. A yellow band left on the alumina column was not further investigated.

Reaction of tert.-*Butyl Hydroperoxide with* 1-*Methylbut*-2-*enyl Phenyl Sulphide.*—The hydroperoxide (2·44 g.) and sulphide (5·0 g.) in benzene (25 ml.) after reaction as above gave water and *tert.*-butyl alcohol (not estimated), a product (1·6 g.), corresponding to product A, of b. p. 30—45°/14 mm., n_D^{20} 1·4230 (Found: C, 71·0; H, 11·5%; *M*, 170), and a crystalline residue (3·1 g.) which after recrystallisation from aqueous alcohol had m. p. 60·0—60·5° and mixed m. p. with diphenyl disulphide 60·3—60·8°.

Reaction of tert.-*Butyl Hydroperoxide with Allyl Phenyl Sulphide.*—No water was isolated from the reaction products of the hydroperoxide (3·43 g.) and sulphide (5·72 g.), and unchanged

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

[12] Wernimont and Hopkinson, *Analyt. Chem.*, 1943, **15**, 272.

sulphide (1·5 g.), b. p. 42—43°/0·01 mm., n_D^{20} 1·5752 (Found : C, 71·8; H, 6·7; S, 21·3. Calc. for $C_9H_{10}S$: C, 72·0; H, 6·7; S, 21·3%), was the only distillable compound apart from *tert.*-butyl alcohol. The major product was a dark viscous residue (4·6 g.) which was dissolved in light petroleum (b. p. 40°) and fractionally eluted from alumina with more solvent (500 ml.). The eluate contained no diphenyl disulphide but left, on removal of the solvent, a small, crystalline, unidentified residue (0·05 g.), m. p. 161—162° (Found : C, 64·6; H, 6·1; S, 19·0%).

Reaction of tert.*-Butyl Hydroperoxide with* n*-Butyl 1-Methylprop-2-enyl Sulphide.*—The products, isolated as described above, from hydroperoxide (6·25 g.) and sulphide (10·0 g.) kept in benzene (50 ml.) *in vacuo* for 100 hr. at 50° ± 0·1° were *tert.*-butyl alcohol (4·35 g.), a sulphur-free product A (0·7 g.), b. p. 30—60°/12 mm. (Found : C, 69·85; H, 12·1%), product B (3·91 g.), b. p. 30—70°/0·01 mm. (Found : C, 56·4; H, 9·85; S, 28·0%), and a residue C (4·39 g.) (Found : C, 52·4; H, 9·3; S, 20·5%). After elution from alumina with light petroleum (b. p. 40°) product B was resolved into slightly impure di-*n*-butyl disulphide (1·95 g.), b. p. 42—44°/0·01 mm., n_D^{20} 1·4928 (Found : C, 54·3; H, 10·2; S, 35·2. Calc. for $C_{18}H_{18}S_2$: C, 53·95; H, 10·1; S, 35·95%. Purity >90%, determined spectroscopically).

Reaction of tert.*-Butyl Hydroperoxide with* n*-Butyl 2-Methylprop-2-enyl Sulphide.*—The hydroperoxide (9·05 g.) and sulphide (14·5 g.) in benzene (100 ml.) were caused to react under the usual conditions, giving *tert.*-butyl alcohol (Found : 7·58 g.; theor., 7·45 g.) and a distillate (14·4 g.), b. p. 34—66°/0·02 mm. (mainly 64—66°). The latter, analysed by Barnard and Hargrave's method,[11] had a purity of 68% as sulphoxide. Shaking with light petroleum (50 ml.; b. p. <40°), in which the sulphoxide is sparingly soluble, followed by the distillation of the insoluble material gave substantially pure (98%) n*-butyl 2-methylprop-2-enyl sulphoxide* (7·85 g.), b. p. 65—66°/0·02 mm., n_D^{20} 1·4885 (Found : C, 59·8; H, 9·9; S, 20·2. $C_8H_{16}OS$ requires C, 60·0; H, 10·0; S, 20·0%). The petroleum solution was run through a column of silica gel (25 g. 100 mesh), followed by more solvent (50 ml.), and the eluate evaporated to an oil (1·2 g.), b. p. 44—45°/0·01 mm., n_D^{20} 1·4939 (Found : C, 53·8; H, 10·0; S, 35·5. Calc. for $C_8H_{18}S_2$: C, 53·95; H, 10·1; S, 35·95%), identified as di-*n*-butyl disulphide from its physical and spectral characteristics.

Reaction of tert.*-Butoxy-radicals with 1-Methylbut-2-enyl Phenyl Sulphide.*—The sulphide (5·0 g.) and di-*tert.*-butyl peroxide (4·1 g.) in chlorobenzene (25 ml.) were degassed *in vacuo* and kept at 115° ± 0·1° under oxygen-free nitrogen for 77 hr. The red solution was diluted with benzene (65 ml.), and the benzene distilled off at atmospheric pressure, then the chlorobenzene at 35 mm. Both were analysed for acetone, *tert.*-butyl alcohol, and di-*tert.*-butyl peroxide content by infrared spectroscopy utilising the bands at 1718, 3580, and 873 cm.$^{-1}$ respectively, the benzene containing all three components and the chlorobenzene only the peroxide (Found : Acetone 0·69 g.; *tert.*-butyl alcohol 2·55 g.; di-*tert.*-butyl peroxide 0·535 g.). The residue (5·1 g.) left after the removal of the solvent contained no component volatile at up to 120°/0·01 mm. other than unchanged sulphide (0·8 g.) and could be only partially distilled in a pot-type " molecular " still at 120°/0·001 mm., to give a golden-yellow distillate (0·66 g.) (Found : C, 73·8; H, 7·0; S, 18·2%; *M*, 270) and a viscous residue [Found : C, 74·0; H, 6·9; S, 17·8; *M*, 520. $(C_{11}H_{13}S)_n$ requires C, 74·6; H, 7·35; S, 18·1%].

I thank Dr. K. R. Hargrave for helpful criticism of this work which forms part of the programme of research undertaken by this Association.

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[*Received, August* 12*th*, 1955.]