

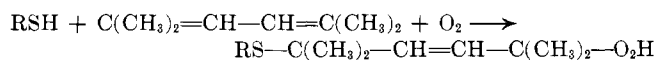
## Organic Sulfur Compounds. XI.<sup>1</sup> Amine-Hydroperoxide Complexes as Intermediates in the Co-oxidation of Thiols with 2,5-Dimethyl-2,4-hexadiene<sup>2</sup>

ALEXIS A. OSWALD,<sup>3</sup> KARL GRIESBAUM, and B. E. HUDSON, JR.*Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey*

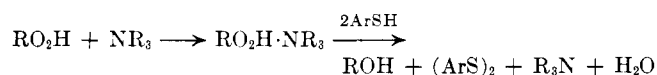
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2,5-Dimethyl-5-arylmercapto-3-hexen-2-yl hydroperoxides (I) react with 1,4-diazabicyclo[2.2.2]octane (II) to form crystalline triethylenediammonium bishydroperoxides (III) as hydrogen-bonded complexes. These hydroperoxide complexes (III) are instantaneously reduced to the corresponding alcohols (V) by aromatic thiols. The free hydroperoxides (I) also are reduced by thiols in the presence of alkylamine catalysts. Due to the formation of such amine-hydroperoxide complexes, thiols and 2,5-dimethyl-2,4-hexadiene are co-oxidized by molecular oxygen in the presence of alkylamines to form the corresponding alcohols (V, VI), disulfides, and water instead of the hydroperoxides (I). Such catalytic action is probably important when hydrocarbon fuels, containing diene and thiol trace components, are stabilized by alkylamines.

It has been reported in a previous paper of this series<sup>4</sup> that thiols and 2,5-dimethyl-2,4-hexadiene are readily co-oxidized by molecular oxygen to form unstable 5-arylmercapto-2,5-dimethyl-3-hexen-2-yl hydroperoxides.



Our earlier studies,<sup>5,6</sup> showed that hydroperoxides form complexes with alkylamines. These complexes react readily with aromatic thiols to yield the corresponding alcohol, disulfide, alkylamine and water.



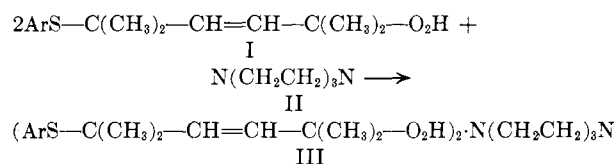
Apparently alkylamines can act as catalysts for hydroperoxide reduction by thiols. By analogy, it seemed probable that olefinic hydroperoxides containing sulfur—as products or intermediates of diene-thiol co-oxidation reactions—would also be readily reduced by thiols in the presence of alkylamines. Such reactions would obviously influence the peroxidation of hydrocarbon fuels containing thiols and diolefins. Therefore, their study was of interest from the viewpoint of the chemistry of fuel instability.

A method for the reduction of hydroperoxides—from conjugated diene-thiols co-oxidation—to the corresponding more stable alcohols was also of interest for the determination of 1,2- and 1,4-isomeric products. Analysis of the structural isomers formed in such co-oxidation reactions could be carried out more conveniently after reduction. The one-step co-oxidation-reduction reported here was then used on other conjugated diolefins to study the factors determining 1,2- vs. 1,4-mechanism of thiol-diene co-oxidations.<sup>7</sup>

### Results

**Amine Complexes of Hydroperoxides from Diene-Thiol Co-oxidation.**—It was found that 2,5-dimethyl-5-arylmercapto-3-hexen-2-yl hydroperoxides (I), from

aromatic thiol-2,5-dimethyl-2,4-hexadiene co-oxidation, also react with alkalamines. When a relatively high melting diamine, 1,4-diazabicyclo[2.2.2]octane (triethylenediamine) (II), was used for complex formation, the resulting triethylene diammonium bishydroperoxides (III) could be isolated as colorless low melting crystals from cold ether and/or *n*-pentane (Table I).



The nuclear magnetic resonance spectra of these amine-hydroperoxide salts (Table II) were very similar to those of the corresponding free hydroperoxides.<sup>4</sup> A typical spectrum is shown in Fig. 1. All these salts show a very characteristic AB quartet in the vinyl region of the spectrum.<sup>8</sup> The magnitude of the coupling constant (15–17 c.p.s.) of the vinyl protons is characteristic of *trans*-internal olefins. The two very strong singlet peaks originate from the two pairs of geminal methyl groups. The 12 equivalent protons of the triethylenediamine component contribute a strong singlet to the spectra of the complexes. The signal of the proton of the hydroperoxy group was not always evident; in some cases it may have been obscured by the multiple signals of the aromatic protons. This suggestion is supported by observations that the hydroperoxy proton generally appears at a lower field than the hydroxyl proton. For instance, the hydroperoxy proton of *t*-butyl hydroperoxide appears at 10 p.p.m., while the hydroxyl proton of the corresponding alcohol shows up at 4 p.p.m.

The infrared spectra of these complexes retained the main characteristic absorption bands of the parent compounds.<sup>4</sup> The originally strong peak of the hydroperoxide at 2.8  $\mu$ , however, occurred only as a weak peak in the complex. In contrast, a broad band of increased intensity was observed around 3  $\mu$ , that is, in the hydrogen-bonding region (Fig. 2). This indicated that these complexes, as expected, are strongly hydrogen-bonded complexes of the following type (p. 2352).

(1) For the previous paper of this series see *J. Am. Chem. Soc.*, **85**, 1969 (1963).

(2) This paper was presented before the Organic Chemistry Division, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(3) Esso Research Center, P. O. Box 45, Linden, N. J.

(4) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, **27**, 2439 (1962).

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(6) A. A. Oswald, F. Noel, and G. Fisk, *ibid.*, **26**, 3974 (1961).

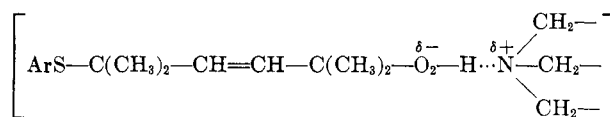
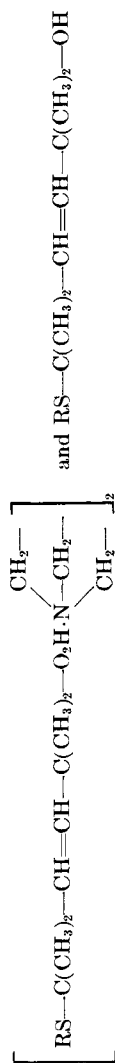
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(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 122, 238.

TABLE I  
TRIETHYLENEDIAMINE SALTS OF HYDROPEROXIDES FROM THIOL-2,5-DIMETHYL-2,4-HEXADIENE CO-OXIDATION BY O<sub>2</sub> AND SOME ALCOHOLS FROM THEIR REDUCTION BY THIOLS

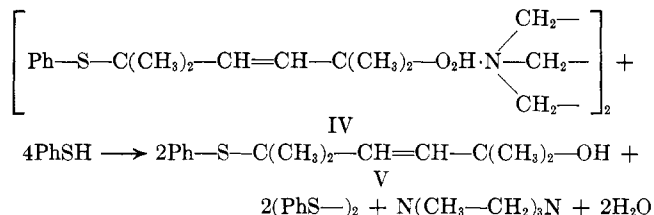
Type	R	Compound		Conversion after, hr.		Product purity, %		Physical data		Elemental analyses, %						
		Formula	Yield, %	%	hr.	Ultra-violet	%	M.p., °C., b.p. (mm.)	n <sub>D</sub> <sup>20</sup>	Calcd.			Found			
Salt	Phenyl	C <sub>24</sub> H <sub>42</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	75	...	No	96 <sup>a</sup>	50-52	...	66.19	8.50	4.54	10.40	65.59	8.31	4.64	9.95
	4-Chlorophenyl	C <sub>24</sub> H <sub>37</sub> ClN <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	83	...	No	96 <sup>a</sup>	81-83	...	59.55	7.34	4.08	9.36	59.46	7.42	4.19	9.10
Alcohol	4-Butylphenyl	C <sub>42</sub> H <sub>68</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	58	...	No	96 <sup>a</sup>	...	...	67.19	9.41	3.84	8.79	67.35	9.65	4.11	8.35
	Methyl	C <sub>9</sub> H <sub>18</sub> OS	94	30	Yes	95 <sup>b</sup>	58-60 (1)	1.4910	62.02	10.41	...	18.39	61.80	10.35	...	18.20
	Ethyl	C <sub>10</sub> H <sub>20</sub> OS	95	28	Yes	95 <sup>b</sup>	72-75 (1)	1.4887	63.77	10.70	...	17.03	63.45	10.88	...	16.89
	Phenyl	C <sub>14</sub> H <sub>26</sub> OS	89	60	No	93 <sup>b</sup>	108-111 (1)	1.5667	71.14	8.53	...	13.56	71.27	8.62	...	13.64

<sup>a</sup> By n.m.r. <sup>b</sup> By capillary gas chromatography. <sup>c</sup> Oxygenation of *n*-heptane solution containing 0.9 mole/l. of thiol and 0.3 mole/l. of diene.



#### Reduction of Hydroperoxide-Amine Salts by Thiols.

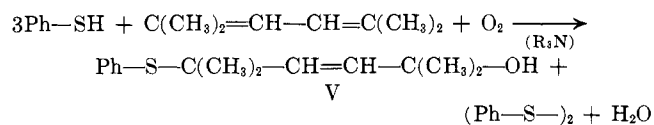
The triethylenediamine salt of the hydroperoxide of benzenethiol-2,3-dimethyl-2,4-hexadiene co-oxidation (IV) reacted with aromatic thiols to yield the corresponding alcohol (V), diphenyl disulfide, and water.



The alcohol was isolated as an odorless, high boiling liquid by fractional distillation at about 1 mm. Its n.m.r. and infrared spectra (Table II, Fig. 1 and 2) were characteristically different from those of the corresponding hydroperoxide amine complex.

The free 5-phenylmercapto-2,5-dimethyl-3-hexen-2-yl hydroperoxide was also reduced by thiols in the presence of only catalytic amounts of triethylenediamine or other aliphatic amines. Amine catalysis probably occurs through the formation of an intermediate amine-hydroperoxide complex that is reactive towards the thiol. On reduction of the hydroperoxide salt to the alcohol (V) the amine is regenerated.

**Co-oxidation of Diene and Reduction of Hydroperoxide in One Step.**—The previously mentioned results suggested that the co-oxidation of benzenethiol and dimethylhexadiene by oxygen and the reduction of the resulting hydroperoxide by benzenethiol in the presence of alkylamines could be carried out in a single operation.



When oxygen was introduced into an *n*-heptane solution containing 0.9 mole/l. of benzenethiol, 0.3 mole/l. of 2,5-dimethyl-2,4-hexadiene, and 0.01 mole of *t*-butyl primary amine catalyst at room temperature, co-oxidation took place readily. Practically all the thiol disappeared within a day. Distillation of the reaction mixture *in vacuo* provided 5-phenylmercapto-2,5-dimethyl-3-hexen-2-ol (V), diphenyl disulfide, and water in equimolar amounts. The amine was recovered.

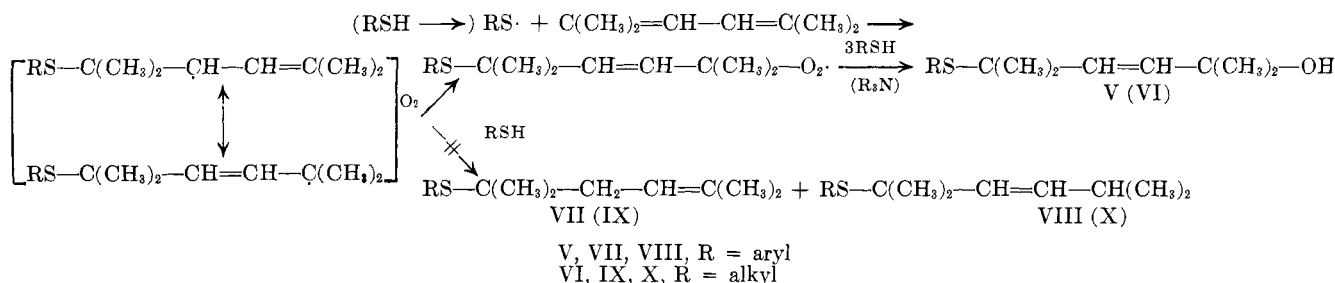
This reaction also can be carried out without any solvent by simply bubbling oxygen into a mixture of the reactant. In this case, however, external cooling is necessary to keep the reaction mixture at room temperature. In the absence of diluents significant amounts of addition products (VII and VIII) are produced besides the co-oxidation products, since the ratio of thiol to oxygen concentration is increased.

Success of the preceding one-step reaction of aromatic thiols suggested a similar combined co-oxidation and reduction reaction using aliphatic thiols and 2,5-dimethyl-2,4-hexadiene. The primary hydroperoxides formed in these latter co-oxidation reactions are unstable liquids and could not be isolated in the pure state.

TABLE II  
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF CO-OXIDATION PRODUCTS OF 2,5-DIMETHYL-2,4-HEXADIENE AND THIOLS

Thiol	Hydroperoxide-amine salt	X (no. of O atoms)	Chemical shifts of structural units, p.p.m., downfield from tetramethylsilane internal reference; s, singlet, t, triplet, q, quadruplet, m, multiplet	$-\text{C}(\text{CH}_3)_2-$	$-\text{CH}=\text{CH}-$	$-\text{C}(\text{CH}_3)_2-$	$\text{O}_2\text{H}$	$\text{N}(\text{CH}_2\text{CH}_2)_2\text{N}$
Benzenethiol	Yes	2	m 7.1-7.6	s 1.26	q 5.48 <sup>a,b</sup>	s 1.18	...	s 2.72
4- <i>t</i> -Butylbenzenethiol	Yes	2	s 7.30, <sup>d</sup> s 1.31 <sup>e</sup>	s 1.36	q 5.42 <sup>a,f</sup>	s 1.18	...	s 2.73
4-Chlorobenzenethiol	Yes	2	q 7.30 <sup>g</sup>	s 1.33	q 5.44 <sup>a,h</sup>	s 1.19	...	s 2.70
Benzenethiol	No	1	m 7.0-7.5	s 1.32	q 5.48 <sup>a,i</sup>	s 1.18	s 3.05	...
Methanethiol	No	1	s 1.82	s 1.30	s 5.45	s 1.26	s 3.75	...
Ethanethiol	No	1	t 1.15, <sup>j</sup> q 2.35 <sup>j</sup>	s 1.33	s 5.58	s 1.28	s 3.60	...

<sup>a</sup> AB type,  $J = 15-17$  c.p.s. <sup>b</sup>  $\delta_{AB} = 0.63$  p.p.m. <sup>c</sup> No n.m.r. resonance was observed. <sup>d</sup> Due to the protons of the 4-substituted phenyl group. <sup>e</sup> Due to the methyl protons of the 4-*t*-butyl group. <sup>f</sup>  $\delta_{AB} = 0.49$  p.p.m. <sup>g</sup> AB type,  $J = 9$  c.p.s.,  $\delta_{AB} = 0.13$  p.p.m. <sup>h</sup>  $\delta_{AB} = 0.47$  p.p.m. <sup>i</sup>  $\delta_{AB} = 0.55$  p.p.m. <sup>j</sup>  $J = 7$  c.p.s.



The reaction is sluggish without initiators, but can be carried to essential completion in a day with ultraviolet irradiation. A "one-pot" reaction of methane- or ethanethiol with 2,5-dimethyl-2,4-hexadiene and oxygen in the presence of *t*-butylamine yielded the expected 1,4-alcohols (VI). Aliphatic thiol-2,5-dimethyl-2,4-hexadiene adduct by-products (IX, X) are absent even when no solvent is used since the reactivity of the intermediate allylic radical is incomparably greater towards oxygen than towards aliphatic thiols.

The 5-alkylmercapto-2,5-dimethyl-3-hexen-2-ols (VI) are, like the corresponding aryl derivative (V), colorless liquids that can be distilled without decomposition *in vacuo*. Their infrared spectra are similar to the alcohol (V) derived from benzenethiol-2,5-dimethyl-2,4-hexadiene co-oxidation. The n.m.r. spectra of the 5-alkylmercapto-2,5-dimethyl-3-hexen-2-ols (VI) (Table II) are also similar, except in the vinyl region. The unsaturated aliphatic alcohols show a singlet in this region whereas the unsaturated aromatic alcohols show an AB-type quartet as do the corresponding hydroperoxides<sup>14</sup> and their amine salts. The appearance of the AB quartet is attributed to the magnetic anisotropy and long range shielding effect of the benzene ring.<sup>9</sup> This creates a magnetic nonequivalence of approximately 0.6-0.7 p.p.m. between the two vinyl protons an otherwise symmetrical magnetic environment. In the case of the aliphatic derivatives the two vinyl protons produce a singlet peak.

**Color Forming Reactions.**—Co-oxidation reactions of reactive unsaturated hydrocarbons, such as conjugated dienes, with thiols by air to form hydroperoxides may be important in color and sediment formation in hydrocarbon fuels. It previously has been reported by Oswald and Noel<sup>10</sup> that the reactions of hydroperoxides with pyrroles (minor constituents of petroleum) lead to the formation of colored substances. It now has been found that *n*-heptane solutions contain-

ing benzenethiol, 2,5-dimethyl-2,4-hexadiene (or other conjugated dienes), and 2,5-dimethylpyrrole become highly colored in a few minutes on aeration in the absence of amine, but remain colorless for days in the presence of tertiary alkyl primary amines. The latter amines ("Primene 81-R," Rohm and Haas Co.) are used as additives in hydrocarbon fuels containing reactive thiols and olefins.<sup>11,12</sup> The results of this and the previously reported studies<sup>5,6</sup> suggest that the stabilizing effect of alkylamines as fuel additives may be partly due to catalysis of hydroperoxide-thiol reaction. In the presence of alkylamines, the hydroperoxides of co-oxidation reaction react with the thiol and not with the pyrroles.

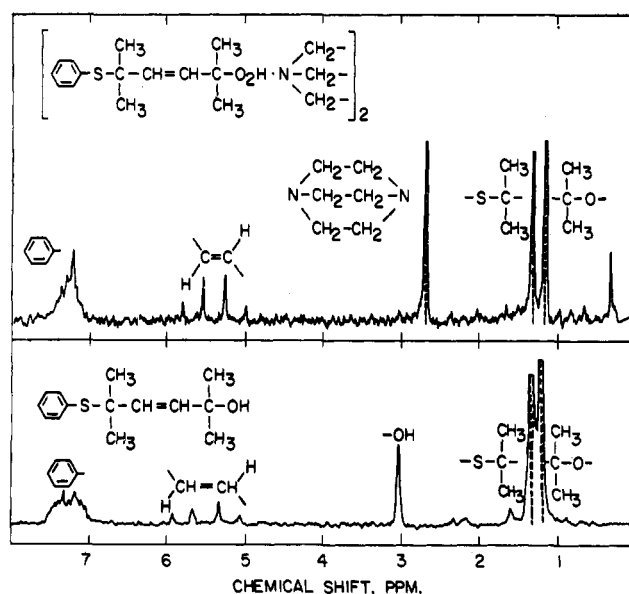


Fig. 1.—Proton n.m.r. spectra of co-oxidation products of benzenethiol and 2,5-dimethyl-2,4-hexadiene.

(11) T. R. Lusebrink, H. B. Minor, A. C. Nixon, and B. M. Steckler, V World Petroleum Congress, Section VI, Paper 12, 1959.  
(12) Esso Research and Engineering Co., German Patent, 941,217.

(9) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).  
(10) A. A. Oswald and F. Noel, *J. Chem. Eng. Data*, **6**, 294 (1961).

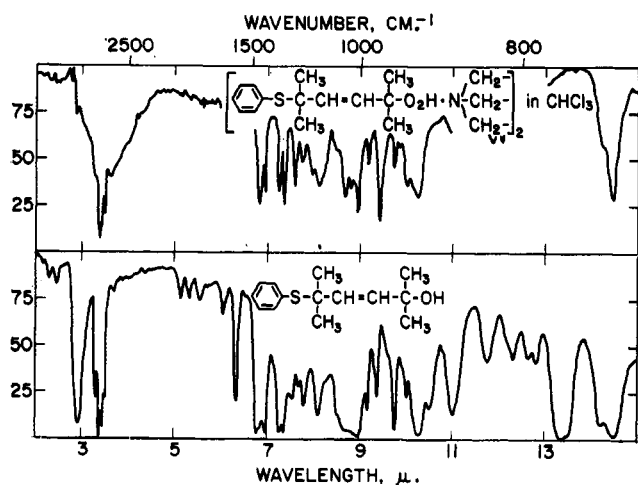


Fig. 2.—Infrared spectra of products of benzenethiol-diene co-oxidation.

### Experimental

**Materials.**—The reactants were purified by recrystallization or distillation before use. The amine catalysts and the solvents were all C.P. reagents. The oxygen used was of a 99.6% purity.

**Methods and Equipment.**—All oxygenations were carried out at atmospheric pressure in a four-neck round bottom flask equipped with a condenser, a dropping funnel, a thermometer, a sintered glass inductor with 7.5-cm.<sup>2</sup> sintered area, and an efficient magnetic stirrer. Oxygen was introduced through a bubbler into the inductor and then into the mixture. It left the conductor through a bubbler. After an initial purging, the oxygen flow rate was adjusted so that about one bubble per second left the reaction mixture.

**Methods of Analyses.**—Hydroperoxide determinations were made by treating the sample with an excess of mercaptan in the presence of *t*-butylamine. The mercaptan consumed was determined by potentiometric back titration with silver nitrate. The progress of the co-oxidation reactions was followed by titrating the unconverted thiols in the reaction mixture. Gas chromatography was generally carried out on an F & M Model 500 linear temperature programmed gas chromatograph using a 10-ft. Carbowax 20 M (20% polyethylene glycol of 20,000 av. mol. wt.) column. The isomeric alcohols of aromatic mercaptan-diolefin co-oxidation were separated on a Barber-Coleman Model 20 capillary chromatograph at 175°, using a 50-ft. column coated

with a substrate consisting of the monoether of tridecyl alcohol and the polyethylene glycol (containing about 30 ethoxy units). N.m.r. spectra were recorded with a Varian Model A-60 proton resonance spectrometer. Infrared spectra were obtained using a Baird recording spectrophotometer, Model B.

**Complex Formation between 5-Arylmercapto-2,3-dimethyl-3-hexene-2-yl Hydroperoxides and Triethylenediamine.**—A saturated pentane solution of 0.05 mole of the hydroperoxide was added to a solution of 2.8 g. (0.025 mole) of triethylenediamine with stirring. The amine salt precipitated instantaneously as colorless crystals; it was isolated by filtration with suction, washed with cold pentane, and dried *in vacuo*. These complexes could also be recrystallized by cooling their pentane or ether solutions.

Some physical and analytical data concerning these complexes are shown in Tables I and II and Fig. 1 and 2.

**Reduction of 5-Phenylmercapto-2,3-dimethyl-3-hexen-2-yl Hydroperoxide Triethylenediamine Salt by 4-*t*-Butylbenzenethiol.**—To an ice-water cooled solution of 16.6 g. (0.05 mole) of the complex in 50 ml. of methanol 16.6 g. (0.1 mole) of 4-*t*-butylbenzenethiol was added dropwise with stirring at or below 10°. An immediate exothermic reaction took place. After the completion of the addition, all the thiol was oxidized within 10 min. The reaction mixture was then cooled to -70° to precipitate most of the oxidation product, bis-4-*t*-butylphenyl disulfide, which was then filtered off with suction and washed with 10 ml. of cold methanol. After drying, 15.8 g. (95%) of bis-*t*-butylphenyl disulfide was obtained.

The filtrate was distilled at atmospheric pressure to remove most of the methanol. The residue was then fractionated at around 1 mm. pressure to yield 8.5 g. (85%) of 5-phenylmercapto-2,3-dimethyl-3-hexen-2-ol as a slightly yellow liquid.

Elemental analyses, physical data, infrared, and n.m.r. spectra of this compound are shown in Tables I and II and Fig. 1 and 2.

**Amine Catalysis of the Reduction of 5-Phenylmercapto-2,3-dimethyl-3-hexen-2-yl Hydroperoxide by 4-*t*-Butylbenzenethiol.**—To an ice-water cooled solution of 11.0 g. (0.05 mole) of the hydroperoxide and 16.6 g. (0.1 mole) of 4-*t*-butylbenzenethiol in 50 ml. of methanol, 0.2 g. (0.03 mole) of *t*-butylamine was added dropwise with stirring. Upon the addition of the amine, an immediate reaction took place as was indicated by the rise of the temperature and by the change of the color of the reaction mixture to yellow (caused by bis-4-*t*-butylphenyl disulfide). After 30-min. stirring, the reaction mixture was worked up in the manner previously described to yield 6.0 g. (96%) of bis-*t*-butylphenyl disulfide and 8.4 g. (82%) of 5-phenylmercapto-2,3-dimethyl-3-hexen-2-ol.

**Acknowledgments.**—The authors wish to thank T. J. Jermansen and T. Vicai for technical help.