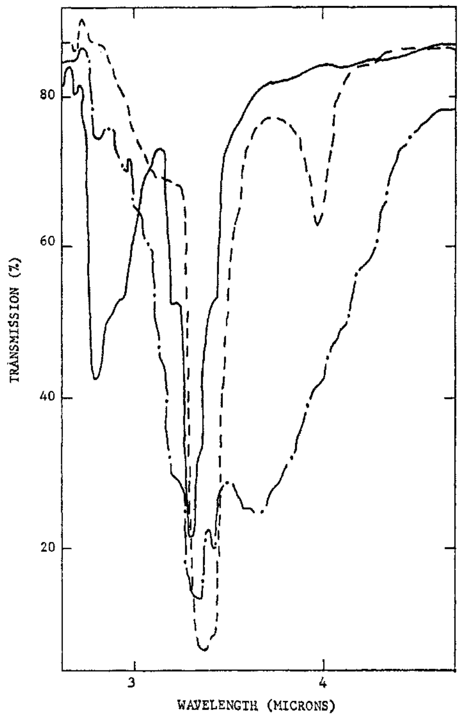

Fig. 2. Infrared spectrum of triethylenediammonium phenylisopropyl peroxide (-·-· in chloroform as compared to that of triethylenediamine (------) and phenylisopropyl hydroperoxide (——)

ethereal solution of 0.05 mole of an aliphatic amine, 0.05 mole of a thiol was added dropwise with shaking. The crystalline precipitate formed was filtered by suction, washed with ether, and dried for 0.5 hr. at 10 mm. in the presence of calcium chloride and paraffin flakes.

Oxygenation of 1,1,3,3-tetramethylbutylammonium 2-naphthalene thiolate. 1,1,3,3-Tetramethylbutylammonium 2-naphthalenethiolate (13 g., 0.044 mole) was dissolved in 4000 ml. of 3:1 benzene:*n*-heptane. The solution was oxygenated in a 5000- ml. measuring cylinder using a sintered glass inductor and stirring. In 6 hr. the mercaptan concentration of the solution decreased to 10% of the original. By concentration *in vacuo* and crystallization, 6 g. (85%) of 2-naphthyl disulfide was obtained. Hydrogen chloride introduction into the mother liquor resulted in the precipitation of 6.6 g. (90%) of 1,1,3,3-tetramethylbutylamine hydrochloride, m.p. 250–254°, identified as 1,1,3,3-tetramethylbutylammonium picrate, m.p. 177–180°.

The amine content of the aerated reaction mixture was also determined by extraction using aqueous hydrochloric acid and was found to be 5.3 g. (93%). The water content of the mixture by the Karl Fischer method was 20 mg./ml. (120%) of the theoretical.

When a solution of 0.84 g. (0.0044 mole) of 2-naphthalenethiol in 100 ml. 3:1 benzene:*n*-heptane mixture was aerated in the absence of amine, the thiol concentration decreased to 87% of the original.

Synthesis of triethylenediammonium alkyl peroxides. A hydrocarbon hydroperoxide (0.05 mole) was added to a solution of 2.8 g. (0.025 mole) of diazabicyclo[2.2.2]octane in 50 ml. of ether. A slightly exothermic reaction took place. The solution was cooled in a carbon dioxide–acetone mixture to crystallize the colorless triethylenediammonium alkyl peroxide which was removed by filtration with suction, washed with cold ether, and dried in a calcium chloride desiccator *in vacuo*. Yields and some physical and analytical data of the products obtained are shown in Tables I and II.

Triethylenediammonium alkyl peroxides can be also synthesized in hydrocarbon solvents or in the absence of any solvent. Toluene and petroleum ether are particularly suitable solvents for the laboratory synthesis of triethylenediammonium phenylisopropyl and tetrahydronaphthyl peroxides, respectively.

Acknowledgment. The authors wish to thank A. Fischel and E. Weiser for the analyses, D. Galbraith and J. Ella for the technical assistance.

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[CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY, ESSO RESEARCH AND ENGINEERING CO. AND FROM THE RESEARCH DEPARTMENT, IMPERIAL OIL LTD.]

Organic Sulfur Compounds. VI. The Effect of Alkylamines on the Course of the Co-Oxidation of Mercaptans and Indene

ALEXIS A. OSWALD,[1a] FERNAND NOEL,[1b] AND GEORGE FISK[1b]

Received December 7, 1960

In the presence of alkylamines, mercaptans and indene are co-oxidized by molecular oxygen with a chain mechanism to form substituted 2-mercapto-1-indanols, disulfides and water, instead of substituted 2-mercapto-1-indanyl hydroperoxides. The initiation reaction forming the mercapto radicals may take place between alkylammonium thiolates and oxygen. The change of the reaction products is due to the catalysis by the amines of the oxidation of mercaptans by substituted 2-mercapto-1-indanyl hydroperoxides. It is proposed that this catalytic action is important in the stabilization of some hydrocarbon fuels by alkylamines.

It has been reported in this series that mercaptans and olefins are readily co-oxidized by molecular oxygen to form substituted 2-mercaptoethyl hydroperoxides.[2]

$$\mathrm{RSH} + \mathrm{CHR'{=}CR_2''} + \mathrm{O_2} \longrightarrow \mathrm{R{-}S{-}CHR'{-}CR_2''{-}O_2H}$$

These hydroperoxides readily rearrange to yield substituted 2-sulfinyl-ethanols.

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[1] (a) Central Basic Research Laboratory, Esso Research and Engineering Co., Linden, N. J. (b) Research Department, Imperial Oil Ltd., Sarnia, Ontario, Canada.

[2] A. A. Oswald, *J. Org. Chem.*, **24**, 443 (1959).

$$R—S—CHR'—CR_2''—O_2H \longrightarrow R—SO—CHR'—CR_2''—OH$$

When co-oxidation reactions were carried out at room temperature, usually only the 2-sulfinylethanols could be isolated.[3,4]

The previous paper of the series[5] described the catalysis of mercaptan oxidation by hydrocarbon hydroperoxides in the presence of aliphatic amines.

$$R'O_2H + 2\ RSH \xrightarrow[(R_3''N)]{} R'OH + RSSR + H_2O$$

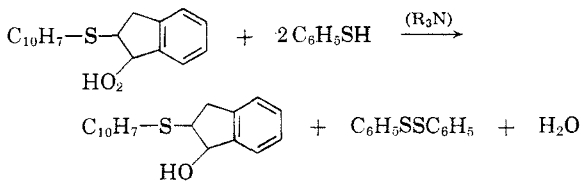
It was proposed that alkylamines act as catalysts by reacting with the hydroperoxides to form alkylammonium peroxides which readily oxidize the mercaptans.

$$R_3''N + R'O_2H \longrightarrow R_3''N\cdot HO_2R'$$

$$R_3''N\cdot HO_2R' + 2\ RSH \longrightarrow R'OH + RSSR + H_2O + R_3''N$$

It seemed probable that hydroperoxides containing sulfur—as products or intermediates of co-oxidation reactions—would also readily oxidize mercaptans in the presence of alkylamines. Such reactions would obviously influence the peroxidation of hydrocarbon fuels containing mercaptans and olefins. Therefore, their study was of interest from the viewpoint of the chemistry of fuel instability.

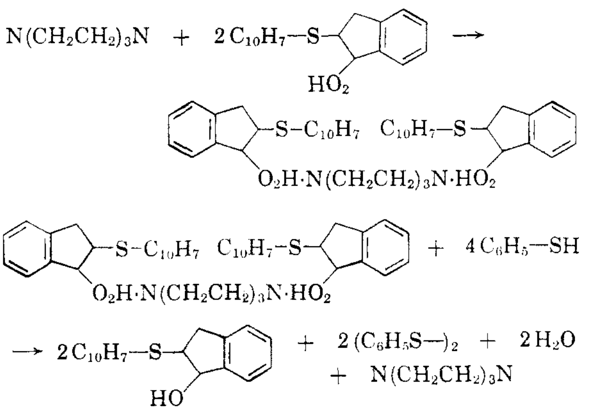
It was found that 2-(2-naphthylmercapto)-1-indanyl hydroperoxide, a relatively stable hydroperoxide containing sulfur, rapidly reacts with benzenethiol in the presence of aliphatic amines to yield bisphenyl disulfide, 2-(2-naphthylmercapto)-1-indanol, and water:



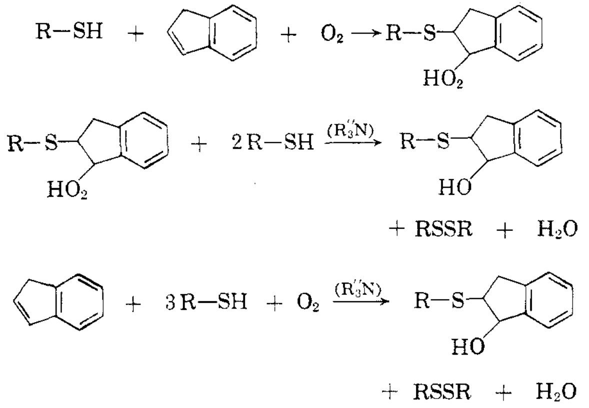
However, the addition of more than an equivalent amount of the above hydroperoxide is necessary in order to oxidize all the thiol. This is due to a side reaction, the rearrangement of the hydroperoxide to 2-(2-naphthylsulfinyl)-1-indanol. In the absence of the amine, no thiol was oxidized.

A similar reaction took place between 2-phenylmercapto-1-indanyl hydroperoxide and benzenethiol in the presence of aliphatic amines. Probably due to instability of this hydroperoxide, the yields of 2-phenylmercapto-1-indanol and bisphenyl disulfide were low.

The aliphatic amines act as catalysts in the usual manner. This is supported by the synthesis of triethylenediammonium 2-(2-naphthylmercapto) 1-indanyl peroxide and by the fast and quantitative reaction of the latter compound with benzenethiol according to the following equation:

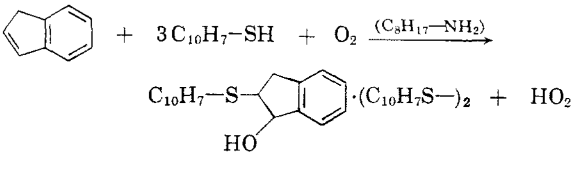


When solutions containing mercaptans and indene were aerated or oxygenated in the presence of an aliphatic amine, co-oxidation and the reaction of the hydroperoxide product with the unchanged thiol both occurred simultaneously. These reactions can be summarized in the following manner:



A complete product analysis of the benzenethiol-indene-1,1,3,3-tetramethylbutylamine system indicates that the above equations correctly represent the main reaction path. When the co-oxidations were carried out in a benzene medium containing 3:1 molar ratio of various aromatic thiols and indene in the presence of 1,1,3,3-tetramethylbutylamine, the corresponding 2-arylmercapto-1-indanols were isolated in fair yields. In most cases no attempt was made to completely recover the disulfide.

The co-oxidation of 2-naphthalenethiol and indene in the presence of 1,1,3,3-tetramethylbutyl-



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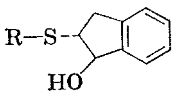
(3) M. S. Kharasch, W. Nudenberg, and G. H. Mantell, *J. Org. Chem.*, **16**, 524 (1951).

(4) J. F. Ford, R. C. Pitkethly, and V. O. Young, *Tetrahedron*, **4**, 325 (1958).

(5) A. A. Oswald, F. Noel, and A. J. Stephenson, *Organic Sulfur Compounds. IV, J. Org. Chem.*, **26**, 3969 (1961).

TABLE I

Synthesis of Substituted 2-Mercapto-1-indanols



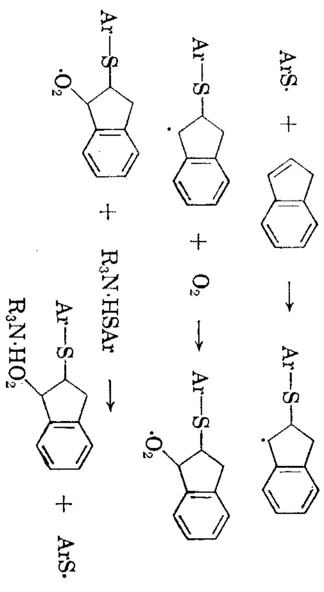
R	M.P.[a]	Calcd.				Found				Yield[b]	Mercaptan Oxidation after 6 Hr., %	Infrared Absorption Peaks, μ				
		C	H	S	OH	C	H	S	OH			OH		Aromatic		
Phenyl	103-104	74.34	5.82	13.23	7.0	74.43	5.91	13.1	6.7	64	58	2.80	2.93	6.22	6.31	
4-Tolyl	95.5-96.5	74.96	6.29	12.51	6.6	74.98	6.45	12.2	6.6	32	95	2.84	2.97	6.23	6.32	
4-Butylphenyl	104-105	76.46	7.43	10.74	5.7	76.52	7.61	10.4	5.7	39	86	2.83	2.97	6.23	6.30	
2-Naphthyl	141-143	78.05	5.52	10.97	5.8	78.01	5.64	10.6	5.6	—	96	2.82	2.96		6.30	
4-Chlorophenyl[c]	113.5-114.5	65.09	4.73	11.58	6.1	65.16	4.92	11.5	6.3	35	75	2.83	2.99	6.23	6.32	6.37
n-Dodecyl	69-72	75.40	10.23	9.59	5.1	75.02	10.35	9.2	—	42	48[d]	2.82	2.95	6.22	6.30	

[a] Uncorrected. [b] Calculated on the basis of the mercaptan oxidized according to the proposed over all reaction equation. [c] Calcd.: Cl, 12.81. Found: Cl, 12.6. [d] After 5 days of oxygenation.

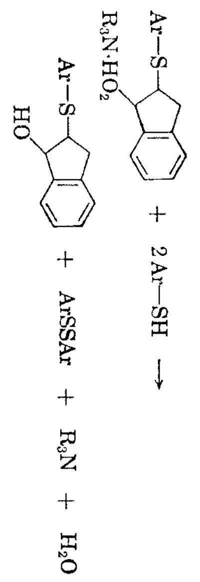
amine yielded the addition product of 2-(2-naphthylmercapto)-1-indanol and bis-2-naphthyl disulfide. The same addition product was formed when triethylenediammonium 2-(2-naphthylmercapto)-1-indanyl peroxide reacted with 2-naphthalenethiol. It also can be produced by the direct addition of 2-(2-naphthylmercapto)-1-indanol to bis-2-naphthyl disulfide.

A comparison of the melting point and infrared spectrum of 2-phenylmercapto-1-indanol with the data of Ford, Pitkethly, and Young[4] indicated that the compound produced by the above reaction was the *trans* isomer. It can be assumed by analogy that the other substituted 2-mercapto-1-indanols obtained were also *trans* isomers. These compounds all crystallized from *n*-heptane in the form of colorless, long, fine needles. On heating, they melted without decomposition. (A number of the corresponding substituted 2-sulfinyl-1-indanols melt with decomposition.[6]) The yields and some physical and analytical data of the compounds obtained are shown in Table I.

No hydroperoxide intermediates could be detected by the potassium iodide test in the presence of alkylamines. The hydroperoxides of the co-oxidation reaction react with the aromatic thiols as quickly as they are formed. It is proposed that very reactive alkylammonium peroxides are formed in the co-oxidation reaction according to the following propagation mechanism:



These peroxide salts react immediately with mercaptans:



An aliphatic thiol, *n*-dodecanethiol, is co-oxidized at a much slower rate with indene in the presence of 1,1,3,3-tetramethylbutylamine to yield the expected 2-*n*-dodecylmercapto-1-indanol.[6]

Aliphatic amines generally do not form salts with aliphatic thiols.[5] Therefore, in this case, the

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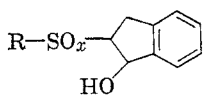
[6] A. A. Oswald, *Organic Sulfur Compounds. III, J. Org. Chem.*, 26, 842 (1961).

TABLE II

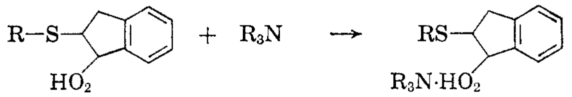
SUBSTITUTED 2-SULFINYL- AND 2-SULFONYLINDANOLS



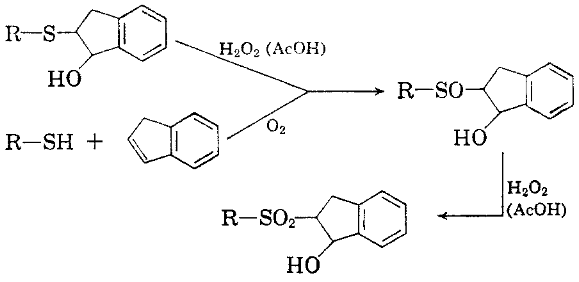
R	x	M.P.[a]	Calcd. C	Calcd. H	Found C	Found H	Yield, %
4-Butylphenyl	1	154–156	72.57	7.05	72.32	7.20	63
n-Dodecyl	1	80–81	71.94	9.78	71.74	9.94	71
4-Tolyl	2	145–146.5	66.64	5.59	66.83	5.65	72
4-Butylphenyl	2	156–158	69.06	6.71	69.03	6.88	98
4-Chlorophenyl	2	151.5–154	58.35	4.24	58.25	4.43	95
n-Dodecyl	2	93.5–94.5	68.81	9.35	68.74	9.42	97

[a] Uncorrected.

formation of the active peroxide salt intermediate takes place by a simple addition of the amine to the hydroperoxide:



The identity of *trans*-2-phenylmercapto-1-indanol was further confirmed by oxidizing it to *trans*-2-phenylsulfinyl- and *trans*-2-phenylsulfonyl-1-indanol. *trans*-2-Phenylsulfinyl-1-indanol can be also prepared by the co-oxidation of indene and benzenethiol in the absence of amine.[4] Other *trans*-2-mercapto-1-indanols have been also oxidized to the corresponding sulfoxides and sulfones. These products are also assumed to have the *trans* structure:



Some properties of the new 2-sulfinyl- and 2-sulfonyl-1-indanols are shown in Table II.

The co-oxidation of benzenethiol and indene was also examined in the presence of various concentrations of 1,1,3,3-tetramethylbutylamine. When the molar concentration of the amine was increased from one hundredth to twice that of the thiol, the rate of mercaptan oxidation increased considerably.

When the amine concentration was equal to or greater than the thiol concentration, the entire thiol was originally present as alkylammonium thiolate.[5,7] The fact that co-oxidation of indene still occurred with the thiolate, suggests that the mercapto anions, from the thiolate, are converted to mercapto radicals. It is proposed that this is due to the reaction of the mercapto anion with molecular oxygen:

$$\mathrm{ArS^- + \cdot O{-}O\cdot \longrightarrow ArS\cdot + \cdot O{-}O^-}$$
$$\mathrm{R_3NH^+ + \cdot O{-}O^- \longrightarrow R_3N\cdot HO{-}O\cdot}$$
$$\mathrm{ArS^- + R_3N\cdot HOO\cdot \longrightarrow ArS\cdot + R_3N\cdot HOO^-}$$
$$\mathrm{R_3NH^+ + R_3N\cdot HOO^- \longrightarrow R_3N\cdot HOOH + R_3N}$$
$$\mathrm{R_3N\cdot HOOH + 2\ RSH \longrightarrow 2\ H_2O + RSSR + R_3N}$$

Similar reactions between carbanions and oxygen have been reported by James and Weissberger,[8] Reid,[9] Russell and Moye[10]:

$$\mathrm{2\ R_3C^- + O_2 \longrightarrow 2\ R_3C\cdot + O_2^{-2}}$$

In a series of experiments, the effect of different types of aliphatic amines on indene-benzenethiol co-oxidation was examined. The results, shown in Table III, indicate that in the presence of mono- and dipropylamine a rapid mercaptan conversion occurred, but the yield of the *trans*-2-phenylmercapto-1-indanol was below the theoretical. From the reaction mixture containing mono-*n*-propylamine, more than the theoretical yield of phenyl di-

TABLE III

CO-OXIDATION OF INDENE AND BENZENETHIOL IN THE PRESENCE OF *n*-PROPYLAMINES

n-Propylamine	Color of Solution After 6 Hr.	Mercaptan Oxidation, %	Yield of 2-Phenylmercapto-1-indanol,[a] %	Yield of Disulfide,[a] %
Mono-	Purple	81	63	110
Di-	Green	81	61	75
Tri-	Yellow	34	96	—

[a] Calculated on the basis of mercaptan oxidized according to the proposed over-all reaction equation.

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[7] G. F. Grillot and T. J. Brooks, Jr., *J. Am. Chem. Soc.*, 72, 4281 (1950).

[8] T. H. James and A. Weissberger, *J. Am. Chem. Soc.*, 60, 99 (1938).

[9] D. H. Reid, *Chem. & Ind.*, 1504 (1956).

[10] G. A. Russell and A. J. Moye, *Preprints Symposia*, 5 (2) C25 (1960), Petroleum Chemistry Division of American Chemical Society, Cleveland Meeting, April 1960.

sulfide was isolated. This suggests that in the presence of this strong base some oxidation to disulfide by molecular oxygen took place. In the presence of tri-*n*-propylamine, the mercaptan conversion was smaller but the reaction was more selective to *trans*-2-phenylmercapto-1-indanol.

Reactions forming color. In all the co-oxidation experiments reported here, observations were made on the color of the reaction mixtures. It was hoped that these observations might help to explain the structural requirements of aliphatic amines as retarders of color formation in hydrocarbon fuels containing reactive mercaptans and olefins.[11,12] When indene was co-oxidized in the presence of 1,1,3,3-tetramethylbutylamine with unsubstituted aromatic thiols—benzene- and 2-naphthalene-thiol—the reaction mixtures turned light yellow. This was apparently due to the formation of the corresponding bisaryl disulfides. Similar mixtures containing 4-*t*-butyl-, 4-methyl- and 4-chlorobenzenethiols turned increasingly dark in this order. It was apparent that the latter thiols took part in some side reaction responsible for the formation of the dark color. Such a side reaction may be the oxidation of thiols to sulfonic acids which subsequently polymerize indene. This, however, was not examined further.

When benzenethiol and indene were co-oxidized in the presence of mono-, di- and tri-*n*-propylamine, color formation was also observed. Cooxidation in the presence of mono- and di-propylamine resulted in a colored reaction mixture within an hour. In the presence of tri-*n*-propylamine or 1,1,3,3-tetramethylbutylamine, less color was formed. It is proposed that this color formation is due to the decomposition of alkylammonium peroxide intermediates formed in the co-oxidation reactions. This is supported by the coloration on decomposition of alkylammonium tetrahydronaphthyl peroxides derived from the same alkylamines and tetrahydronaphthyl hydroperoxide.[5] Again the derivatives of mono- and di-*n*-propylamine formed the most color. 1,1,3,3-Tetramethylbutylamine and tri-*n*-propylamine derivatives remained colorless for a longer time. These observations can be explained by the decreased reactivity of the latter amines due to the *t*-alkyl group and the tertiary nitrogen, respectively. A study of the decomposition of alkylammonium peroxides is in progress.

It has been previously reported by Oswald and Noel[13] that the reactions of hydroperoxides with pyrroles lead to the formation of colored substances. These reactions may be important in color and sediment formation in hydrocarbon fuels. *n*-Heptane solutions containing benzenethiol, indene and 2,5-dimethylpyrrole became highly colored in a few minutes on aeration in the absence of amine, but remained colorless for days in the presence of tertiary alkyl primary amines. The results of this and the previously reported study[5] indicate that the stabilizing effect of alkylamines as fuel additives may be partly due to the catalysis of hydroperoxide-mercaptan reaction. In the presence of alkylamines, the hydroperoxides of co-oxidation reaction react with the mercaptan and not with the pyrroles.

EXPERIMENTAL

Materials. The liquid mercaptans, olefins, and alkylamines were vacuum distilled under nitrogen before use. The solid mercaptans were recrystalized from *n*-heptane.

Experimental procedure. In the co-oxidation experiments, the oxygen or air was introduced through a sintered glass inductor into the bottom of the reaction mixture. The mixture was magnetically stirred in a three neck, round bottom flask fitted with a water cooled condenser which was connected to a trap cooled by solid carbon dioxide–acetone bath. The pressure in the reaction vessel was kept slightly above atmospheric. The reactions were followed by determining the decrease of the thiol concentration by potentiometric titration of samples with silver nitrate using a silver-glass electrode.

Reaction of 2-(2-naphthylmercapto)-1-indanyl hydroperoxide with benzenethiol in the presence of 1,1,3,3-tetramethylbutylamine. To a solution of 14.2 g. of 65% 2-(2-naphthylmercapto)-1-indanyl hydroperoxide (0.03 mole) in 2500 ml. of toluene, 6.6 g. (0.06 mole) of benzenethiol and 7.6 g. (0.06 mole) of 1,1,3,3-tetramethylbutylamine were added. The resulting reaction mixture turned yellow immediately (indicating disulfide formation) and was allowed to stand for 0.5 hr. A subsequent thiol determination indicated that 12% of the thiol remained unchanged. Less than the theoretical thiol was consumed, probably because of the rearrangement of 2-(2-naphthylmercapto)-1-indanyl hydroperoxide to 2-(2-naphthylsulfinyl)-1-indanol as a side reaction.

The solution was concentrated *in vacuo.* At first, small, heavy, colorless crystals of 2-(2-naphthylsulfinyl)-1-indanol precipitated which were filtered off. Then all the solvent was distilled, leaving a brownish residue. From this residue, 1,1,3,3-tetramethylbutylamine and bisphenyl disulfide were removed by leaching with two 60-ml. portions of 5% aqueous hydrochloric acid and three 25-ml. portions of *n*-heptane, respectively. The remaining raw 2-(2-naphthylmercapto)-1-indanol (9.2 g., m.p. 130–133°) was recrystallized from toluene to yield 5.2 g. (56%) of pure product as long, light, needle-like, colorless crystals, m.p. 141–143°. Analytical data of the purified product are shown in Table I.

Reaction of 2-phenylmercapto-1-indanyl hydroperoxide with thiophenol in the presence of 1,1,3,3-tetramethylbutylamine. To a solution of 13.2 g. (0.12 mole) of benzenethiol and 7.7 g. (0.06 mole) of 1,1,3,3-tetramethylbutylamine in 250 ml. of benzene, 19.4 g. of frozen pieces of 79% 2-phenylmercapto-1-indanyl hydroperoxide was added with stirring. The solution was stirred for another hour after the addition. Then the solvent was removed *in vacuo.* The colored residue was fractionally crystallized from heptane to yield 5 g. (34%) of 2-phenylmercapto-1-indanol, m.p. 103–104° (see Table I) and 4.2 g. (32%) of bisphenyl disulfide, m.p. 60–61°.

Triethylenediammonium 2-(2-naphthylmercapto)-1-indanyl peroxide. A solution of 6.3 g. (0.02 mole) of 2-(2-naphthylmercapto)-1-indanyl hydroperoxide in 25 ml. of ether was added slowly to a solution of 1.1 g. (0.01 mole) of triethylenediamine in 10 ml. of ether. An immediate exothermic reaction took place with the precipitation of colorless, fine,

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[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 Pat. 941,217.

[13] A. A. Oswald and F. Noel, *Role of Pyrroles in Fuel Instability, Chem. Eng. Data,* 6, 294 (1961).

powder-like crystals. These were filtered off, washed with two 20-ml. portions of ether, and dried to yield 6.7 g. (91%) of triethylenediammonium 2-(2-naphthylmercapto)-1-indanyl peroxide, m.p. 89–90°.

Anal. Calcd. for $C_{44}H_{44}N_2O_2S_2$: C, 72.50; H, 6.08; N, 3.84; Peroxide equiv., 182. Found: C, 72.61; H, 6.22; N, 3.95; Peroxide equiv., 195.

The synthesis can be also carried out in a similar manner in toluene, which is a much better solvent for the product.

Reaction of triethylenediammonium 2-(2-naphthylmercapto)-1-indanyl peroxide with benzenethiol. To a solution of 1.1 g. (0.01 mole) of benzenethiol in 80 ml. of toluene, 1.8 g. (0.0025 mole) of triethylenediammonium 2-(2-naphthylmercapto)-1-indanyl peroxide was added slowly with stirring. The resulting yellow mixture was allowed to stand for 0.5 hr., filtered to remove the water formed, then cooled by a solid carbon dioxide-acetone mixture and filtered while cold. The white, crystalline substance obtained was recrystallized from toluene to yield 1.2 g. (83%) of 2-(2-naphthylmercapto)-1-indanol, m.p. 141–143°.

Reaction of triethylenediammonium 2-(2-naphthylmercapto)-1-indanyl peroxide with 2-naphthalenethiol. To a solution of 6.4 g. (0.04 mole) of 2-naphthalenethiol in 50 ml. of toluene, 7.3 g. (0.01 mole) of triethylenediammonium 2-(-naphthylmercapto)-1-indanyl peroxide was added slowly with stirring. The resulting bluish green mixture was allowed to stand for 0.5 hr., cooled by an ice water mixture, and filtered by suction. The precipitate isolated was recrystallized from toluene to yield 8.8 g. (97%) of 2-(2-naphthylmercapto)-1-indanolbis-2-naphthyl disulfide addition product. The product was obtained in the form of almost colorless crystals which melted at 126–127° while turning yellow.

Anal. Calcd. for $C_{39}H_{30}OS_3$: C, 76.68; H, 4.95; S, 15.75. Found: C, 76.41; H, 5.13; S, 14.9.

Addition product of 2-(2-naphthylmercapto)-1-indanol and bis-2-naphthyl disulfide. 2-(2-Naphthylmercapto)-1-indanol (1.46 g., 0.005 mole) and 1.6 g. (0.005 mole) of bis-2-naphthyl disulfide were dissolved in 25 ml. of toluene by heating on the water bath. The solution was allowed to cool to room temperature. The crystals formed were filtered by suction and washed with pentane to yield 2.5 g. (80%) of the addition product, m.p. 126–127°.

Co-oxidation of aromatic thiols and indene in the presence of alkylamines. A 333-ml. benzene solution of 0.34 mole of aromatic thiol, 0.11 mole of indene and 0.01 mole of an alkylamine was oxygenated for 6 hr. at 22–28°. By the end of 6 hr., the mixture became colored.

When benzene- and 2-naphthalenethiols were co-oxidized with indene in the presence of 1,1,3,3-tetramethylbutylamine, a yellow color developed. With 4-butylbenzenethiol, the mixture became dark yellow, with 4-toluenethiol, and 4-chlorobenzenethiol, it became red and black respectively. When benzenethiol and indene were co-oxidized in the presence of mono-, di-, and tri-*n*-propylamines, the formation of purple, green, and yellow colors was observed.

After the oxygenation, the benzene phase was decanted from the water which was formed during the reaction. The unchanged thiol was removed from the benzene solution by washing it with 100 ml. of 5% aqueous potassium hydroxide solution. Then the solvent was distilled and the residue was fractionally recrystallized from *n*-heptane to yield long, fine, needle-like crystals, of 2-arylmercapto-1-indanols. The bis-aryl disulfides were too soluble in *n*-heptane and therefore, were recrystallized from methanol.

In the case of the 2-naphthalenethiol-indene co-oxidation, the reactant concentrations were reduced to one-third of the above and benzene was used for recrystallization because of the smaller solubility of the reaction product; the addition compound of 2-(2-naphthylmercapto)-1-indanol and bis-2-naphthyl disulfide.

The co-oxidation of benzenethiol and indene in the presence of 1,1,3,3-tetramethylbutylamine was also carried out on a five times larger scale in toluene to separate the water and the amine. After 6 hr. of oxygenation, 58% of the thiol was oxidized and 4.4 g. (85%) of water separated. By the extraction of the reaction mixture with two 100-ml. portions of 5% aqueous hydrochloric acid, and the concentration of the extract, 7 g. (85%) of tetramethylbutylammonium hydrochloride, m.p. 150–154°, was isolated. The latter was identified as tetramethylbutylammonium picrate, m.p. 178–180°. Workup of the toluene solution in the usual manner resulted in the isolation of 20.5 g. (73%) of 2-phenylmercapto-1-indanol.

Co-oxidation of n-dodecanethiol and indene in the presence of 1,1,3,3-tetramethylbutylamine. An *n*-heptane solution (333 ml.) of 73.3 g. (0.33 mole) of *n*-dodecanethiol, 22.9 g. (0.22 mole) of indene, and 4.2 g. (0.033 mole) of 1,1,3,3-tetramethylbutylamine was oxygenated at 24–26°. When the thiol content of the solution decreased to 53% of the original (5 days), the reaction product was isolated by fractional crystallization. The yield and some physical and analytical data of the product are shown in Table I.

Oxidation of 2-arylmercapto-1-indanols to 2-arylsulfinyl-1-indanols. To a solution of 0.01 mole of 2-arylmercapto-1-indanol in acetic acid, 1.1 g. of 33% aqueous hydrogen peroxide (0.0105 mole) was slowly added at about 50° with shaking. Where necessary, more acetic acid was added to yield a clear solution at this temperature. The reaction mixture was then kept at 60° for 0.5 hr. to complete the reaction.

The resulting 2-arylsulfinyl-1-indanol was precipitated by the careful addition of water to the reaction mixture. Then it was filtered off and further purified by recrystallization from ethanol. Some physical and analytical data of the new 2-(4-butylphenylmercapto)-1-indanol prepared are shown in Table II. Most of the oxidation products were identified with one (presumably the *trans*) isomer of the substituted 2-sulfinyl-1-indanols from the co-oxidation of indene with the corresponding thiol in the absence of amine[5] as is shown in the following:

-thiol Starting Compound	2-Sulfinyl-1-indanol Obtained by H_2O_2 Oxidation, M.P.
Benzene	147–148.5 dec.
Toluene	144–145.5 dec.
4-Chlorobenzene	146.5–148 dec.
2-Naphthalene	134.5–136
n-Dodecane	80–81

Oxidation of 2-arylmercapto-1-indanols to 2-arylsulfonyl-1-indanols. An acetic acid solution of 0.01 mole of 2-arylmercapto-1-indanol was oxidized with 2.3 g. of 33% aqueous hydrogen peroxide (0.022 moles) as described above. The workup of the reaction mixtures, after heating for 1 hr. at 80°, yielded the 2-arylsulfonyl-1-indanols shown in Table II.

Co-oxidation of benzenethiol and indene in the presence of various concentrations of 1,1,3,3-tetramethylbutylamine. Benzene solutions (100 ml. each) containing 0.15 mole/l. of benzenethiol and 0.05 mole/l. of indene were oxygenated in the presence of various concentrations of 1,1,3,3-tetramethylbutylamine at room temperature. After 6 hrs. of oxygenation, the following decrease in mercaptan percentage was observed:

Amine (Mole/L.)	Thiol Oxidized, %
Nil	41
0.015	14
0.150	48
0.300	47

Co-oxidation reactions in the benzenethiol-indene-2,5-dimethylpyrrole system in the presence and in the absence of tertiary alkyl primary amines. Primene 81-R (a mixture of C_{12-15} tertiary alkyl primary amines supplied by the Rohm and Haas Co.) was added to *n*-heptane solutions containing benzenethiol, indene, and 2,5-dimethylpyrrole. The test solutions (300 ml. each) were aerated for 6 hr. at room temperature and the following observations were made:

Benzenethiol, Indene, 2,5-Dimethylpyrrole, (Mole/L., Each)	Primene 81-R, (Mole/L.)	Thiol Oxidized, %	Peroxide Formed	Color of Solution	Precipitate, (G./100 Ml.)
0.30	Nil	68	Yes	Red	3.5 (Red oil)
0.30	0.03	56	No	Colorless	1.3 (Colorless crystals)[a]
0.01	Nil	75	Yes	Red	0.2 (Red solid)
0.01	0.001	53	No	Colorless	None

[a] Identified as *trans*-2-phenylmercapto-1-indanol.

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Preparation of Dithiooxamide Derivatives

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A number of *N,N'*-disubstituted dithiooxamides were synthesized by two methods: (1) reactions of aliphatic primary amines or the salts of amino acids with dithiooxamide; (2) treatment of an oxamide with phosphorus pentasulfide. *N,N'*-Disubstituted dithioxamides containing carboxyl or hydroxyl groups underwent esterification reactions without alteration of the thioamido grouping. Several polymeric dithiooxamides were obtained by the reactions of diamines with dithiooxamide. Limitations to the use of the first method in the preparation of *N,N'*-disubstituted dithiooxamides were found. Infrared spectra of *N,N'*-disubstituted dithiooxamides are reported for the first time and discussed.

Relatively few dithiooxamides are recorded in the chemical and patent literature, but an extraordinarily wide range of applications has been claimed for them. They have shown promise as effective metal deactivators in petroleum products.[2] They have been found to act as vulcanization accelerators.[3] Several of them have demonstrated inhibiting actions on certain bacteria[4] and dehydrogenases[5] Dithiooxamide itself has been used in the syntheses[6] of fluorescent 2,2'-dithiazoles that may be useful histological agents.[7] Dithiooxamides characteristically form stable metal complexes[8] that have been shown to act as color sources in duplicating processes[9,10] and as molecularly oriented, dichroic stains in light-polarizing films.[11] The versatility of this class of compounds has prompted us to synthesize a number of new dithiooxamide derivatives, many of which are listed in the tables. Three synthetic routes were utilized to obtain these compounds: (1) condensation of primary aliphatic amines with dithiooxamide; (2) treatment of oxamides with phosphorus pentasulfide; and (3) esterification of either *N,N'*-bis(carboxymethyl)dithioxamide or *N,N'*-bis(2-hydroxyethyl)-dithiooxamide.

The general reaction of unsubstituted thioamides with primary aliphatic amines under mild reaction conditions, referred to hereafter as the Wallach reaction,[12] has often been used to prepare *N*-alkyl-

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