94% ethanol (prepared by diluting 6% of water by volume with absolute ethanol to the mark). The reaction mixture for the 5% reaction was prepared by diluting 250 ml. of the solution with 250 ml. of 0.4 M sodium ethoxide in absolute ethanol; that for the 100% reaction was prepared by diluting 15 ml. of the solution with 15 ml. of 1 M sodium ethoxide in absolute ethanol. Solutions were equilibrated in the constant-temperature bath prior to mixing, and addition of base was done with the apparatus completely connected to prevent loss of any methyl sulfide. The system was maintained at a pressure of ca. 100 mm., and the reaction bottle at 24° in the 5% reaction. After 5.5 min. the reaction was quenched with 110 ml. of 1 M aqueous HCl, and nitrogen passed through the mixture for another hour to expel products. The 100% reaction was run in a similar fashion for 1.5 hr. at ca. 170-mm. pressure and 35°.

2. The E1 Reaction.—The apparatus was the same as for the E2 reaction. Solutions were prepared in the same manner, except the 0.1 M solutions in 94% ethanol were diluted with equal values of absolute ethanol to give the final reaction mixtures. The 5% reaction was conducted at 40° for 3.8 hr. and a partial vacuum of 170 mm. The 100% reaction was conducted at 75° for 3 hr. at atmospheric pressure.

Purification of Dimethyl Sulfide Samples.—The collection trap was connected to a vacuum line and the sample distilled through a tube containing phosphorus pentoxide into a small sample tube. The material collected in this tube was transferred with a chilled hypodermic syringe to a gas chromatograph (Wilkins Aerograph Model A-90C) fitted with a 5-ft. column of 20% tri-o-cresyl phosphate on Chromosorb. At room temperature and a flow rate of 25 ml. per min. the retention time for isobutylene was 1.5 min. and for dimethyl sulfide 17 min. The latter peak was collected in a trap immersed in liquid nitrogen. In the SN1–E1 reactions another peak followed shortly after the dimethyl sulfide (probably t-butyl alcohol or t-butyl ethyl ether) but could be separated from it satisfactorily. The dimethyl sulfide was then distilled into the sample bulb and carefully degassed as described before.[3]

Mass Spectrometry.—A Consolidated Model 21-620 instrument was used. The procedure was similar to that used before.[3] Sample pressure was normally 300 μ. Some dependence of the apparent mass 62:mass 64 ratio on sample pressure was noted. A set of runs on the same pair of 100 and 5% samples over the range 150–300 μ showed no significant variation in the isotope effect, provided the two samples of a pair were measured at the same pressure. This was accomplished by starting each series of runs at the same scale deflection on the recorder, and carrying out the 20 consecutive scans on a rigidly timed schedule. The 100% sample was run both before and after the 5% sample. The standard deviations from the mean of the averages of 20 scans usually were less than 0.2%.

Kinetic Measurements.—Apparatus and sampling techniques were similar to those used by Williams.[4] Solvents and solutions were prepared as described above (Preparation of Samples for Measurement of Mass Spectra). Temperature control was good to ±0.05°, and temperatures were checked against an N.B.S. thermometer. Chilled aliquots from the SN1–E1 reaction were titrated with standard base. Aliquots from the E2 reaction were quenched in 0.1 N hydrochloric acid and back titrated with standard base. No particular effort was made to attain maximum precision. Most of the rate constants are good to ±5% or better, but those for the faster reactions may be as poor as ±10%.

Organic Sulfur Compounds. XIV.[1] Oxidative Addition of Thiol Acids to Unsaturated Hydrocarbons. Cooxidation of Thiolacetic Acid and Indene by Molecular Oxygen

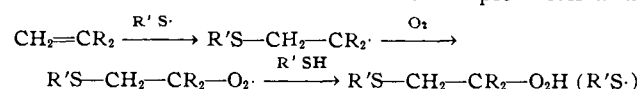BY ALEXIS A. OSWALD,[2] KARL GRIESBAUM, AND WALTER NAEGELE

RECEIVED MARCH 13, 1964

The mechanism of oxidative addition of thiol acids to unsaturated hydrocarbons was studied with thiolacetic acid and indene as model reactants. While the free-radical addition of thiolacetic acid to indene is a rather slow process, a rapid chain reaction occurs when solutions containing thiolacetic acid and indene are oxygenated at room temperature. In the cooxidation reaction, the 2-acetylmercaptoindanyl radical (V) resulting from addition of the acetylmercapto radical to indene combines with ·O₂· to form a peroxy radical (VII). This then abstracts hydrogen from thiolacetic acid to yield the unstable 2-acetylmercapto-1-indanyl hydroperoxide (VIII), a new type of peroxide compound, as the primary cooxidation product. The hydroperoxide VIII is slowly reduced by thiolacetic acid or thiols to the corresponding alcohol IX. Aliphatic amines catalyze this reduction. The structures of the new addition and cooxidation products (VI, VIII, and IX) were established by n.m.r. and infrared spectroscopy. An analogous cooxidation mechanism seems applicable to the oxidative addition of thiolcarboxylic and thiophosphoric acids to olefinic hydrocarbons and anthracenes and opens a new synthetic route to β-acylmercaptoalkanols.

Introduction

The cooxidation of thiolacetic acid and hydrocarbons—anthracenes[3,4] and fluorenes[4]—with molecular oxygen was first described by Mikhailov and Blokhina in 1951. Ten years later, Beckwith and Beng See[5] reexamined the reaction of thiolacetic acid with anthracene and oxygen. On cooxidation with anthracene, Mikhailov and Blokhina[3,4] obtained diacetyl disulfide and the two isomeric 9,10-dihydro-9,10-bis(acetylmercapto)anthracenes (IV) as the main products. Beckwith and Beng See found[5] that 9-acetylmercapto-

anthracene (III) and some sulfur were also formed. Each group proposed a different reaction mechanism. We believe that the chain mechanism proposed by the second group is the more probable one. This mechanism postulates 9,10-dihydro-9-acetylmercapto-10-hydroperoxyanthracene (I) as the primary and 9,10-dihydro-9-acetylmercapto-10-hydroxyanthracene (II) as the secondary unstable reaction products. This mechanism for thiolacetic acid cooxidation is analogous to the mechanism of cooxidation of simple thiols and

$$CH_2{=}CR_2 \xrightarrow{\;R'S\cdot\;} R'S{-}CH_2{-}CR_2\cdot \xrightarrow{\;O_2\;}$$

$$R'S{-}CH_2{-}CR_2{-}O_2\cdot \xrightarrow{\;R'SH\;} R'S{-}CH_2{-}CR_2{-}O_2H \;(R'S\cdot)$$

(1) Previous paper of this series, *J. Am. Chem. Soc.*, **86**, 2877 (1964).

(2) Central Basic Research Laboratory, Esso Research and Engineering Co., Esso Research Center, P. O. Box 45, Linden, N. J.

(3) B. M. Mikhailov and A. N. Blokhina, *Dokl. Akad. Nauk, S.S.S.R.*, **80**, 373 (1951).

(4) B. M. Mikhailov and A. N. Blokhina, *Problemy Mekhanizma Org. Reaktsii, Akad. Nauk, Ukr. S.S.R.; Oldel. Fiz.-Mat. i Khim. Nauk*, 215 (1953); *Chem. Abstr.*, **50**, 16,735f (1956).

(5) A. L. J. Beckwith and Low Beng See, *J. Chem. Soc.*, 1304 (1961).

(6) A. A. Oswald, *J. Org. Chem.*, **24**, 443 (1959); **26**, 842 (1961); A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *ibid.*, **27**, 2439 (1962).

(7) A. A. Oswald, F. Noel, and G. Fisk, *ibid.*, **26**, 842 (1961).

(8) For a more detailed treatment of this subject, see A. A. Oswald and T. J. Wallace, "Anionic Oxidation of Thiols and Co-oxidation of Thiols and Olefins by Molecular Oxygen," chapter in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, London, in press.
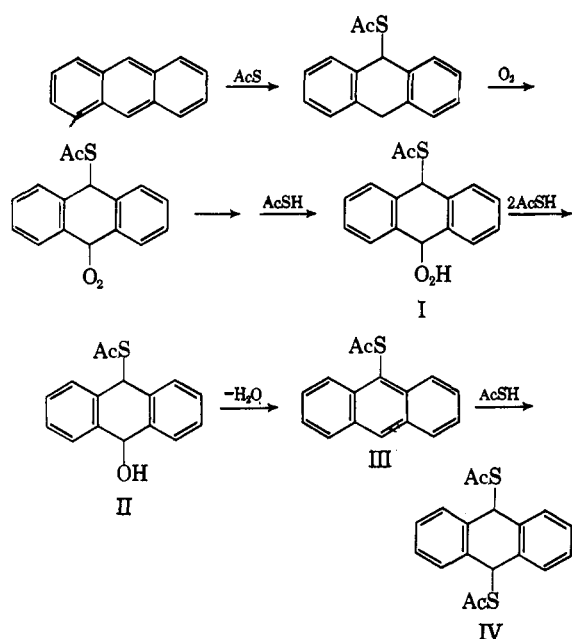
olefins that had been studied previously in our laboratory.[6-8]

In the present paper we describe the results of our study of the cooxidation of thiolacetic acid and indene by molecular oxygen which support the above mechanism of thiolacetic acid–hydrocarbon cooxidations by the isolation of the initial hydroperoxide (VIII) and the subsequent alcohol (IX) cooxidation product.

In conjunction with this cooxidation study, the closely related radical addition of thiolacetic acid to indene was also examined (Table I). A comparative nuclear magnetic resonance (n.m.r.) spectroscopic study of the new cooxidation and addition products obtained was also made (Fig. 1) to confirm their structures.

Results

Addition.—In the absence of oxygen, thiolacetic acid was found to add slowly to indene to yield quantitatively 2-acetylmercaptoindane ,(VI), a colorless
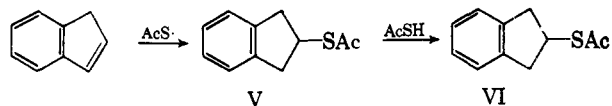
solid which could be distilled *in vacuo* without decomposition. *t*-Butyl hydroperoxide and ultraviolet light catalyze the reaction (Table I), indicating that it pro-

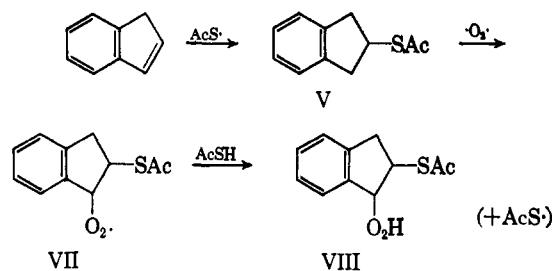TABLE I

CATALYSIS OF THIOLACETIC ACID ADDITION TO INDENE[a]

Catalyst	Thiolacetic acid reacted, %[b]
None	45
t-Butyl hydroperoxide[c]	79
Ultraviolet light[d]	95
Oxygen[e]	89

[a] *n*-Heptane solutions containing thiolacetic acid and indene, both in 0.4 mole/l. concentration, were stored for 17 hr. at room temperature. [b] Determined by subtracting the thiolacetic acid left after 3 hr. from the original amounts. [c] 0.075 mole/l. [d] From 5-cm. distance through cooling water by a Hanau laboratory immersion lamp #313. [e] On oxygenation solid 2-acetylmercapto-1-indanyl hydroperoxide cooxidation product precipitated from the solution.

ceeds by a radical mechanism through a 2-mercaptoindanyl radical (V) intermediate.

Cooxidation.—Oxygenation of solutions containing thiolacetic acid and indene, each about 0.3 mole/l. concentration, resulted in a rapid, exothermic cooxidation. In an aliphatic hydrocarbon solvent, such as heptane, the reaction was practically complete after 3-hr. oxygenation at room temperature with most of the cooxidation product precipitated as a colorless solid. Ultraviolet light was an effective catalyst for the cooxidation, indicating a radical type reaction with a chain mechanism.

The structure of the isolated cooxidation products depended upon the reaction temperature. When the oxygenated reaction mixture was irradiated with ultraviolet light at −15° for 6 hr., a small amount of a solid melting at 48–50° precipitated as the only product from the cooxidation mixture. The solid gave a positive hydroperoxide test by the iodide method. Quantitative hydroperoxide group analysis by the thiol method,[7] infrared absorption spectroscopy, and elemental analyses indicated that it is the monohydrate of the expected primary cooxidation product 2-acetylmercapto-1-indanyl hydroperoxide (VIII). The hydroperoxide VIII after isolation turned into a brown solid on standing at room temperature. In chloroform solution, however, it was fairly stable.

The hydroperoxide could be reduced by the thiol method[7,9,10] with 2-naphthalenethiol in the presence of an aliphatic amine catalyst to yield the corresponding alcohol, 2-acetylmercapto-1-indanol (IX)
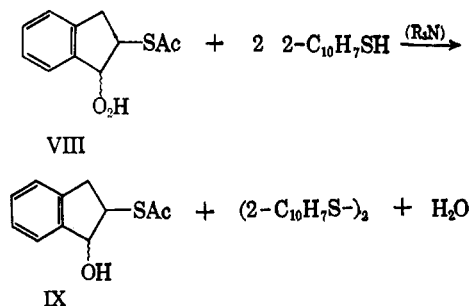

This alcohol is more stable than the hydroperoxide. It melts without decomposition at 119.5–120.5°.

When the cooxidation reaction was carried out at a higher temperature, 5°, the precipitate consisted of the 2-acetylmercapto-1-indanyl alcohol (IX) and the hydroperoxide VIII with some adsorbed diacetyl disulfide. Product analysis made it apparent that at 5°

(9) A. A. Oswald, F. Noel, and A. J. Stephenson, *J. Org. Chem.*, **26**, 3969 (1961).

(10) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 2351, 2355 (1963).

<div align="center">TABLE II</div>

<div align="center">PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF THIOLACETIC ACID–INDENE ADDITION AND COOXIDATION PRODUCTS</div>
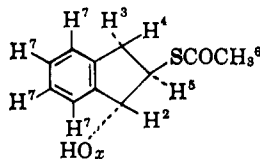

<div align="center">Chemical shifts for the various protons in deuteriochloroform solution (about 10%) downfield from tetramethysilane internal reference,</div>

<div align="center">p.p.m.: s, singlet; d, doublet; q, quartet; m, multiplet; b, broad peak</div>

x	H^1	H^2	H^3	H^4	H^5	H_x^6	H_x^7
0	q $2.88^{b,c,d}$	q $3.45^{b,d,f}$	q $2.88^{b,c,d}$	q $3.45^{b,d,f}$	m $4.24^{c,f,i}$	s 2.30	s 7.15
2^a	b 5.63	d 5.38^g	q $2.83^{j,l,m}$	q $3.57^{j,k,m}$	m $4.40^{g,k,l,n}$	s 2.35	m 7.1-7.6
1	s $3.0-3.5^e$	d 5.13^h	q $2.79^{j,i,p}$	q $3.44^{j,o,p}$	m $3.90^{h,n,o}$	s 2.35	m 7.1-7.5

^{a} Probably present as the monohydrate, $\delta H_2O = 6.6$ p.p.m. ^{b} A or B part of an A_2B_2X spin system. ^{c} $J_{1,5} = J_{3,5} = 6.5$ c.p.s. ^{d} $J_{1,2} = J_{3,4} = 16$ c.p.s. ^{e} δOH is strongly dependent on the concentration. ^{f} $J_{2,5} = J_{4,5} = 7.5$ c.p.s. ^{g} $J_{2,5} = 4.5$ c.p.s. ^{h} $J_{2,5} = 6$ c.p.s. ^{i} X part of an A_2B_2X spin system. ^{j} A or B part of an ABXY spin system, J_A and $J_{BY} = 0$ c.p.s. ^{k} $J_{4,5} = 8$ c.p.s. ^{l} $J_{3,5} = 6.5$ c.p.s. ^{m} $J_{3,4} = 17$ c.p.s. ^{n} X part of an ABXY spin system. ^{o} $J_{3,5} = J_{4,5} = 8$ c.p.s. ^{p} $J_{3,4} = 16$ c.p.s.

most of the primary hydroperoxide cooxidation product VIII reacted with the still unreacted thiolacetic acid according to this equation.[11]

+

2AcSH

+

$(AcS-)_2$ + H_2O
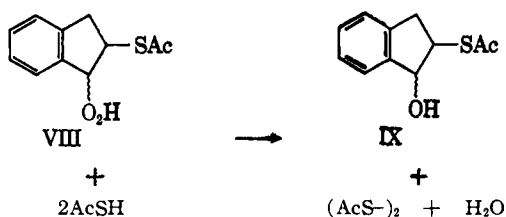
The water obtained in this latter reaction apparently forms a monohydrate with the hydroperoxide. This course of the reaction was further substantiated by using methanol—which is a better solvent for the hydroperoxide than n-heptane—as a reaction solvent. From the homogeneous methanol reaction medium only the alcohol was isolated. The same result was also obtained in n-heptane, if the cooxidation was carried out in the presence of an alkylamine, which apparently catalyzes the reduction of the hydroperoxide by the excess thiolacetic acid.

N.m.r. Studies.—Comparative n.m.r. studies confirmed the proposed structures of the addition and cooxidation products of thiolacetic acid and indene (VI, VIII, and IX, Fig. 1 and Table II).

In all these products, the methyl protons of the mercaptoacetyl group appear as a singlet signal with almost identical chemical shifts. The aromatic protons of all the compounds also appear in the same spectral region; however, a singlet signal is observed for the aromatic protons of the adduct and a multiplet for those of the cooxidation products.

In each product, the methylene protons on the α-carbon show a characteristic eight-line pattern. The two geminal protons have different chemical shift values (δ_A and δ_B) since they are stereochemically nonequivalent by virtue of their cis and trans relationships to the substituent on the β-carbon atom. The resulting AB quartet[12a] is split again by spin coupling to the proton on the β-carbon. The four inner lines of the re-

sulting pattern are more intense than the two pairs of outer lines because the coupling constant J_{AB} is of comparable value to the difference in chemical shifts[12b] ($J_{AB}/\delta_{AB} = 0.4$). This assignment of the eight-line pattern is supported by the intensities observed; this part of the spectrum corresponds to 4 protons in the adduct and only 2 protons in the cooxidation products.

Comparison of the α-methylene region of the spectrum of the adduct (which has two pairs of α-methylene protons) with that of indane (where all four α-methylene protons are equivalent) shows that one pair of methylene protons of the adduct and the four α-methylene protons of indane have identical chemical shift positions (2.88 and 2.86 p.p.m., respectively). The downfield shift (by 0.56 p.p.m.) of the other pair of methylene protons of the adduct can be explained in terms of a long range negative shielding effect, owing to the diamagnetic anisotropy of the carbonyl bond in the mercaptoacetyl group.[12c] As shown by a molecular model of the adduct, this deshielding effect of the carbonyl group affects only those α-hydrogens which are in a cis position to the mercaptoacetyl group. Accordingly, the second lower field quartet (3.45 p.p.m.) has been assigned to these protons. The coupling constant of these lower field protons is larger than that of the trans protons with the methine proton on the β-carbon atom ($J_{2,5} = J_{4,5} = 7.5$ vs. $J_{1,5} = J_{3,5} = 6.5$ c.p.s.). Since the coupling constant for trans-vicinal protons should be larger,[13,14] this is a further support for their assignment. The β-methine proton H^5 is split into a five-line pattern by the 4 α-methylene protons of the adduct.

The spectra of the cooxidation products differ characteristically from that of the adduct. Owing to the effect of the hydroperoxy and the hydroxy group, the expected doublet of the proton on the α-carbon (H^2) is shifted downfield by about 2.25 p.p.m. for the hydroperoxide and 2.0 p.p.m. for the alcohol. The methine proton of the β-carbon, in both compounds, exhibits a multiplet due to the different coupling constants with the three vicinal protons. The chemical shift values for the hydroxyl, hydroperoxide, and hydrate protons are dependent on concentration, solvent, etc. The intensity ratio of the hydroperoxide vs. hydrate protons is, however, exactly 1 : 2.

(11) A more detailed study of thiolacetic acid oxidation by hydroperoxide, to be published in this series, revealed a competing reaction yielding acetic acid and sulfur.

(12) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y.: (a) pp. 82–111, (b) pp. 89–90, (c) p. 123.

(13) M. Karplus, J. Chem. Phys., 30, 11 (1959).

(14) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, J. Am. Chem. Soc., 80, 6098 (1958).

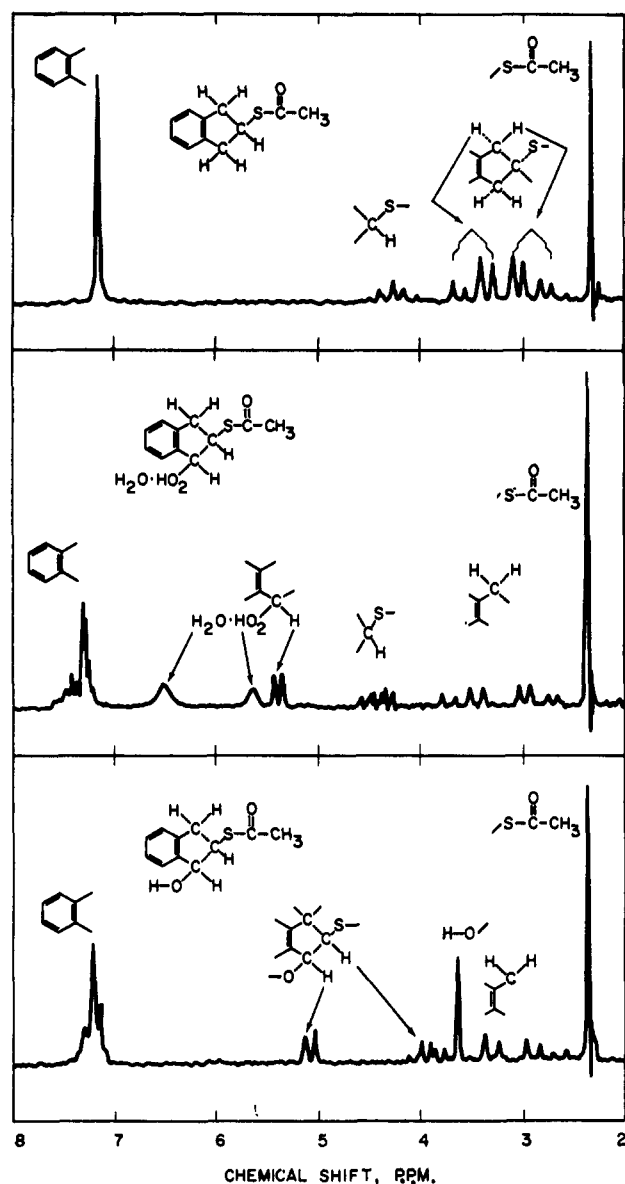Fig. 1.—Nuclear magnetic resonance spectra of thiolacetic acid–indene addition and cooxidation products in CDCl₃ with (CH₃)₄Si internal standard (0 p.p.m.)

Discussion

Thiolacetic acid and indene were readily cooxidized in solution by molecular oxygen at room temperature to yield 2-acetylmercapto-1-indanyl hydroperoxide (VIII) as the primary cooxidation product. This in turn was reduced by thiolacetic acid to the corresponding alcohol IX.
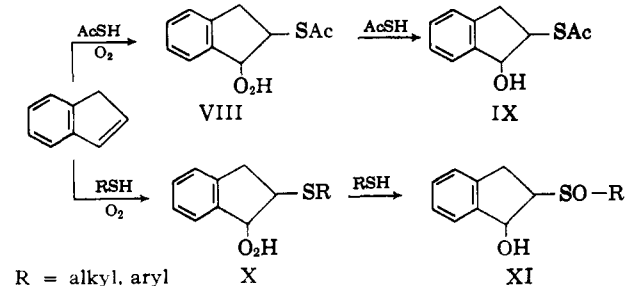
The primary hydroperoxide product of the thiolacetic acid–indene cooxidation (VIII) was apparently

analogous to the respective cooxidation products of simple thiols and indene (X). However, the hydroperoxide from the thiolacetic acid (VIII) cooxidation is very different in its oxidation–reduction behavior. It reacts with the unreacted thiolacetic acid even in the absence of any amine catalyst. In contrast, the hydroperoxides from thiol cooxidations (X), in the absence of catalyst, rearrange to the corresponding hydroxy-ethyl sulfoxides (XI).[6]

The trans structure of the indene–thiol cooxidation products (XIV) indicated that the reaction of the 1-indanyl radical intermediate with oxygen occurred in a stereospecific trans manner. Structural analysis of the indene–thiolacetic acid cooxidation products VIII and IX by n.m.r. and infrared spectroscopy is in agreement with a similar stereochemical formulation of both reactions.

X = CH₃CO, alkyl, aryl
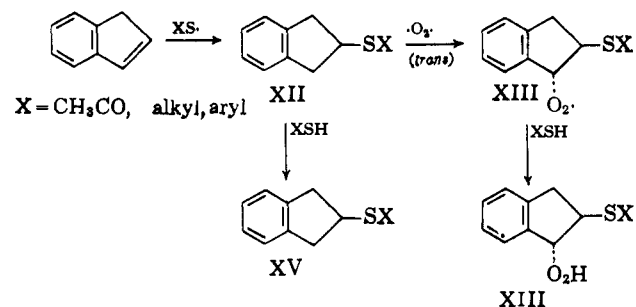
In the cooxidation reaction, the intermediate indanyl radical (XII) instantaneously combines with the oxygen diradical in a reaction of no significant activation energy.[15,16] The peroxy radical formed (XIII) then abstracts a hydrogen from the thiol present to yield the hydroperoxide XIV. In the side reaction, the same indanyl radical (XII) abstracts a hydrogen—in a comparatively slow reaction of significant activation energy[17,18]—to form the adduct XV.

Exploratory experiments indicate that the above cooxidation reaction of thiolacetic acid with indene can be extended to other mono- and diolefins.

Experimental

Materials and Methods.—The thiolacetic acid and the indene were distilled under nitrogen before use. The oxygen was of 99.6% purity. An n.m.r. spectrum of the thiolacetic acid indicated the presence of about 2% acetic acid. Spectra of the reaction mixtures indicated that the acetic acid was not consumed. The disappearance of the thiolacetic acid during the reactions was followed by potentiometric titration with silver nitrate using a silver glass electrode. The hydroperoxide formed was determined by the mercaptan method.

The n.m.r. spectra (Fig. 1, Table I) were recorded with a Varian Model A-60 proton resonance spectrometer using tetramethylsilane as internal standard and deuteriochloroform as solvent. The infrared spectra (Table III) were obtained in chloroform solution using a Baird recording spectrophotometer, Model B.

The oxygenations were carried out at atmospheric pressure in a four-neck flask equipped with a sintered-glass inductor with 7.5-cm.² sintered area, a magnetic stirrer, a thermometer, and a dropping funnel. After an initial purging, the oxygen flow was adjusted so that about one bubble of gas left the reaction mixture per second.

Addition of Thiolacetic Acid to Indene.—To 11.6 g. (0.1 mole) of indene, in a quartz flask, 7.6 g. (0.1 mole) of thiolacetic acid
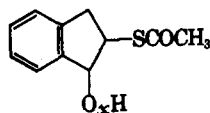
(15) D. E. Hoare and A. D. Walsh, Trans. Faraday Soc., 53, 1102 (1957)
(16) L. Bateman, Quart. Rev. (London), 8, 147 (1954.)
(17) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.
(18) A. A. Oswald, J. Org. Chem., 25, 467 (1960).

TABLE III

CHARACTERISTIC INFRARED ABSORBTION PEAKS OF THIOLACETIC ACID–INDENE ADDITION AND COOXIDATION PRODUCTS

X, number of O atoms	O—H		C—H		C=O		7.xx	7.5	8.2	8.6	8.9	9.55	9.8	10.x	10.5
							(C=O stretching and OH deformation included)								
0			3.4 sm	3.5 sm	5.95 vs	6.00 vs	7.40 s		8.2 s	8.6 i	8.9 vs		9.8 m	10.2 s	10.5 vs
2	2.85 sm	2.95 s	3.4 m	3.5 m		5.95 vs	7.35 s	7.5 m	8.2 s	8.6 i	8.9 vs	9.55 m	9.8 m	10.3 s	10.5 vs
1	2.85 m	2.95 s	3.4 m	3.5 w	5.95 vs	6.00 vs	7.40 s		8.2 s	8.6 s	8.9 vs	9.55 s	9.8 s	10.4 s	10.5 vs

Absorption peaks (vs, very strong; m, medium; i, inflection) in chloroform solution. Stretching region. Fingerprint region.

was added dropwise with stirring under nitrogen. When no apparent reaction occurred, the mixture was irradiated with ultraviolet light. This results in an immediate exothermic reaction. The reaction temperature was kept below 30° by cooling with running water. The reaction was 95% complete in 20 hr.

Fractional distillation of the reaction mixture *in vacuo* yielded 13 g. (95% based on the thiolacetic acid reacted) of 2-acetylmercaptoindane (V) as a colorless liquid boiling from 113–114° at 2 mm. On standing, the distillate turned into a solid melting at 41–43°.

Anal. Calcd. for $C_{11}H_{12}S$: C, 68.71; H, 6.29; O, 8.32; S, 16.68. Found: C, 68.67; H, 6.28; O, 8.18; S, 16.82.

2-Acetylmercapto-1-indanyl Hydroperoxide (VIII) by Cooxidation at −15°.—A solution of 23 g. (0.3 mole) of thiolacetic acid and 34.8 g. (0.3 mole) of indene in a mixture of 800 ml. of *n*-heptane and 200 ml. of toluene was oxygenated at −15° with ultraviolet irradiation in a quartz flask for 6 hr. The reaction mixture was then filtered by suction, and the colorless, crystalline precipitate washed with *n*-pentane to obtain 4.2 g. (6.2%) of 2-acetylmercapto-1-indanyl hydroperoxide hydrate, m.p. 48–50°.

Anal. Calcd. for $C_{11}H_{14}SO_4$: C, 54.53; H, 5.82; S, 13.23. Found: C, 51.14; H, 5.79; S, 14.12. It is believed that the low carbon and high sulfur content found are due to sulfur impurity.

The filtrate from the reaction mixture was fractionally distilled to yield 24.2 g. (42%) of 2-acetylmercaptoindane addition product, 3 g. (13.1%) of diacetyl disulfide, and 9.5 g. (27.3%) of unchanged indene.

2-Acetylmercapto-1-indanol (IX) from the Hydroperoxide.—To a solution of 1.6 g. (0.01 mole) of 2-naphthalenethiol reducing agent and 01040 g. (0.0005 mole) of *t*-butylamine catalyst in 40 ml. of methanol, 1.2 g. (0.005 mole) of 2-acetylmercapto-1-indanyl hydroperoxide was added with stirring at −5°. Upon the dissolution of the hydroperoxide, precipitation of a bis-2-naphthyl disulfide started. After standing for 1 hr., this precipitate was filtered off with suction, washed with methanol, and vacuum-dried to yield 1.3 g. (81%) of bis-2-naphthyl disulfide, identified by its infrared spectrum. The filtrate was concentrated, filtered, and dried to yield 0.9 g. (90%) of 2-acetylmercapto-1-indanol (IX), identified by its n.m.r. spectrum. On recrystallization from methanol, this yielded 0.7 g. of the pure indanol, m.p. 120.5–121.5°.

Anal. Calcd. for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.80; S, 15.40. Found: C, 63.25; H, 5.73; S, 15.17.

2-Acetylmercapto-1-indanyl Hydroperoxide and Alcohol by Cooxidation at 5°.—To an ice–water cooled solution of 34.8 g. (0.3 mole) of indene, 500 ml. of *n*-heptane in 23 g. (0.3 mole) of thiolacetic acid was added with effective oxygenation and stirring. Oxygenation of the stirred reaction mixture was continued at 5° for 5 hr. In an hour, a colorless, crystalline precipitate formed. After 5 hr., the reaction mixture was filtered with suction and washed twice with 50-ml. portions of cold *n*-pentane and air-dried to yield 14.8 g. of a solid product. Semiquantitative n.m.r. analysis of this solid showed that it consisted of 9.8 g. (48%) of 2-acetylmercapto-1-indanol, 3.3 g. (5%) of 2-acetylmercapto-1-indanyl hydroperoxide, and 1.2 g. (4%) of diacetyl disulfide with some trace impurities.

Fractional distillation of the filtrate yielded 4.4 g. (19.5%) of unreacted thiolacetic acid, 16.9 g. (48.5%) of unreacted indene, and 10.7 g. (18.5%) of 2-acetylmercaptoindane adduct by-product.

A similar cooxidation procedure, when run at room temperature, also yielded a peroxidic product. Cooxidation in methanol, under similar conditions, yields a hazy (from colloidal sulfur) but homogeneous reaction mixture, which on concentration yields 2-acetylmercapto-1-indanyl alcohol, in a similar yield but peroxide free.

2-Acetylmercapto-1-indanol by Cooxidation in the Presence of *t*-Butylamine.—A solution of 25.1 g. (0.3 mole) of 90% thiolacetic acid in 475 ml. of *n*-heptane was placed into a round-bottom flask equipped with a gas inductor, a dropping funnel, a thermometer, and a magnetic stirrer. To the solution 0.73 g. (0.01 mole) of *t*-butylamine and then 11.6 g. (0.1 mole) of indene were added with oxygenation and stirring. In 24 hr. of oxygenation, 81% of the thiolacetic acid was consumed and needle-like crystals were formed in the reaction mixture. By filtration with suction, subsequent washing of the crystals with pentane, and drying, 12.5 g. (74% on the basis of the thiol consumed) of 1-(2-acetylmercapto)indanol, m.p. 120.5–121.5°, was isolated.

On distillation of the filtrate *in vacuo*, 8.5 g. (68.5%) of diacetyl disulfide, b.p. 60–65° (1 mm.), and 9.5 g. (22%) of 2-acetylmercaptoindane (VI) were obtained.