Periodate oxidation. For oxidation, 100 mg. of sugar was dissolved in 50 ml. of water, 50 ml. of 0.3*M* solution of sodium periodate added, and the mixture kept at 25° in the dark. Formic acid was liberated with 0.05*N* sodium hydroxide solution added in 5-ml. aliquots. Maximum amounts were formed in 3 days.

To test for formaldehyde, 10 ml. of the final oxidation mixture was distilled at 60° under reduced pressure to collect 7 ml. of distillate in a receiver at 0°. One milliliter of fuchsin sulfurous acid was added and after 10 min. 1 ml. of concd. hydrochloric acid was added. While D-glucose gave a positive blue color, both anhydrides gave a negative test.

Periodate oxidation also produced as one end product an ether which could be characterized. To accomplish this, anhydrides I and II were separately oxidized in 685-mg. quantities with 5.1 g. of sodium meta-periodate in 50 ml. of water. After 5 hr. at 25°, 5 ml. of 2*N* sodium hydroxide solution was added, followed by an excess of sodium borohydride. Reduction was allowed to occur at 25° for 2 hr. and at 45° for 2 hr. The solution was made acid with 2*N* sulfuric acid and neutralized with sodium hydroxide solution. Water was removed by distillation under reduced pressure and the dry residue was extracted several times with absolute tetrahydrofuran. The combined extracts were dried over anhydrous sodium sulfate and concentrated to 10 ml. To this was added 1.4 g. of 2,4-dinitrobenzoyl chloride and 1 ml. of dry pyridine and the mixture was heated 30 min. at 70°. After filtration and distillation to dryness under reduced pressure, the residue was dissolved in warm benzene. This solution was washed first with 2*N* sodium hydroxide solution and then with water and was dried over anhydrous sodium sulfate. The diester crystallized on addition of ether. After recrystallization from a mixture of five parts of heptane and one part of dioxane the melting point was 154°, undepressed on admixture with the authentic sample prepared below. The compounds were also identical in infrared and x-ray patterns.

The authentic sample of β,β'-dihydroxyethyl ether di-2,4-dinitrobenzoate was prepared from a commercial sample of β,β'-dihydroxyethyl ether as described above. Rast mol. wt., 510; calcd., 494.

Anal. Calcd. for $C_{18}H_{14}N_4O_3$: C, 43.73; H, 2.85; N, 11.33. Found: C, 43.82; H, 2.94; N, 11.03.

Hydrolysis of anhydrides I and II. Approximately 5 mg. of anhydride was mixed with 1 ml. of 48% hydrobromic acid and the solutions were heated in a sealed tube for 15 min. at 100°. The contents were diluted with 10 ml. of water and 2 ml. of ethanol. An excess of silver carbonate was added, the mixture filtered and the filtrate treated with hydrogen sulfide. After admixture with carbon, the solution was filtered and concentrated under reduced pressure to a sirup which was taken up in 1 ml. of water. This solution was analyzed by paper chromatography using Whatman No. 1 paper, ethyl acetate–pyridine–water (10:4:3 v/v) as the irrigant and silver nitrate solution as the spray reagent. Anhydride I gave only one hydrolysis component, which had a flow rate equivalent to that of D-glucose. Anhydride II gave evidence of two components in what by visual comparison appeared to be equal amounts, one with the flow rate of D-glucose and one with the flow rate of D-galactose.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, IMPERIAL OIL LIMITED]

Organic Sulfur Compounds. IV.[1a] Some Addition and Co-oxidation Reactions of 4-Chlorobenzenethiol with Dicyclopentadiene and Aldrin

ALEXIS A. OSWALD[1b] AND FERNAND NOEL

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4-Chlorobenzenethiol readily adds to *exo*- and *endo*-dicyclopentadienes and Aldrin (VIII) by a radical mechanism to yield the *exo* and *endo* isomers of 4-chlorophenylmercaptodihydrodicyclopentadiene (IV and V) and 2-*p*-chlorophenylmercapto-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (IX). When 4-chlorobenzenethiol solutions were air oxidized with any of the above diolefins, unstable hydroperoxide intermediates (XIII, XVI, XVIII) were obtained. The hydroperoxide intermediate of the thiol-Aldrin co-oxidation, 2-*p*-chlorophenylmercapto-3-hydroperoxy-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XVIII) was isolated as a colorless, crystalline substance. In solution, it rearranged to the corresponding 2-*p*-chlorophenylsulfinyl-3-hydroxy derivative (XIX). It is suggested that similar co-oxidation and not addition reactions of thiols and dicyclopentadiene are responsible for gum formation in some cracked gasolines.

The results of investigations of radical type mercaptan-olefin addition and co-oxidation reactions[1a,2] suggested that similar reactions of diolefins and mercaptans may occur. The examination of diolefin-mercaptan addition and co-oxidation was of interest from the viewpoint of gum formation in cracked gasolines. Early studies, summarized by Ellis[3] and Gruse[4] concluded that diolefins cause

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[1] (a) A. A. Oswald, *J. Org. Chem.* 26, 842 (1961). (b) Present address: Central Basic Research Laboratory, Esso Research and Engineering Co., Linden, N. J.

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

[3] C. Ellis, *The Chemistry of Petroleum Derivatives*, The Chemical Catalogue Co., Inc., N. Y., (1934) Vol. I, pp. 893–903.

[4] W. A. Gruse, "Gum in Gasoline," Section in Vol. II, p. 1016 of *The Science of Petroleum*, Oxford University Press, London–New York (1938).

rapid gum formation in gasolines because they peroxidize and polymerize readily. Schultze[5] found that the addition of dicyclopentadiene to a "motor spirit" increased gum formation. Kruber and Schade[6] suggested that the deleterious effect of mercaptans on "motor benzene" stability was due to their addition to cyclopentadiene and dicyclopentadiene. The latter compounds are common components in very severely cracked naphtha.[7] Our studies of mercaptan-dicyclopentadiene addition and oxidation of the addition product suggested that the formation of relatively stable sulfides by the mercaptan diolefin addition does not explain why mercaptans are such effective promoters of gum formation. Therefore, the co-oxidation of diolefins and mercaptans was also studied to obtain a better explanation for these and related phenomena.

In the first part of our studies, *endo*-dicyclopentadiene (I), which is formed by the spontaneous dimerization of cyclopentadiene at room temperature,[8] was chosen as a diolefin with isolated double bonds. A reactive aromatic mercaptan, 4-chlorobenzenethiol, was selected for the experiments because aliphatic mercaptans were too sluggish to react with dicyclopentadiene in the absence of catalysts. The reactivity of 4-chlorobenzenethiol is comparable to the toluenethiols normally found in cracked petroleum distillates.

A. *Addition reactions.* 1. *Dicyclopentadiene-4-chlorobenzenethiol.* The possibility of addition of thiols to *endo*-dicyclopentadiene was first mentioned by Kruber and Schade in 1933.[6] They recovered a high boiling oil of 14.8% sulfur content, presumably ethylmercaptodihydrodicyclopentadiene from a mixture of ethanethiol and dicyclopentadiene after standing for fourteen days. Bruson and Riener in 1945[9] reported that the addition of mercaptoacetic acid to dicyclopentadiene gave carboxymethylmercaptodihydrodicyclopentadiene. However, the above authors did not examine the mechanism of the addition.

Cristol and Brindell[10] found that *p*-toluenethiol readily adds to norbornene (bicyclo[2.2.1]-hept-2-ene) by a radical mechanism. When equimolar amounts of norbornene and cyclohexene were allowed to compete for *p*-toluenethiol the product distribution indicated that norbornene is about forty-five times as reactive towards the *p*-tolyl mercapto radical as is cyclohexene.

In this laboratory, it was found that an equimolar amount of 4-chlorobenzenethiol readily adds to *endo*-dicyclopentadiene (I) in a nitrogen atmosphere to yield a light yellow liquid sulfide (IV), which can be distilled *in vacuo* without decomposition. The addition is exothermic even in the absence of any catalyst. The same addition products can be obtained by catalysis with a peroxide (*e.g. t*-butyl hydroperoxide) or ultraviolet light (Table I). Therefore, it is proposed that the addition proceeds by a radical mechanism.

Two moles of 4-chlorobenzenethiol could not be added to one mole of dicyclopentadiene in the absence of catalyst. The second mole of thiol remained unchanged. This showed that normally only one double bond of the dicyclopentadiene takes part in the addition reaction. Differences between the reactivities of the two double bonds in the dicyclopentadiene molecule were reported in the literature. The double bond of the bicycloheptene system was found to be more active in the addition of phenylazide,[11] nitrosyl chloride,[12,13] hydrogen,[11,14,15] bromine,[16,17] water,[18] and various acids,[11,19-21] alcohols and phenols[9] to dicyclopentadiene.

The addition of phenylazide to dicyclopentadiene and derivatives was examined by Alder and Stein[11,22] and was found to take place very readily with compounds containing the bicyclo[2.2.1]-heptene group. The lack of phenylazide addition to dihydrodicyclopentadiene, for example, was used to prove the absence of the bicycloheptene group. In a similar manner in our work, the absence of reaction between the 4-chlorobenzenethiol-dicyclopentadiene addition product and phenylazide indicated that the addition reaction took place at the double bond of the bicycloheptene part of dicyclopentadiene.

Another problem, associated with the structure of the addition product, is the possibility of stereoisomerization to the so-called *endo* and *exo* forms. The *endo*-dicyclopentadiene is formed exclusively when cyclopentadiene is dimerized. On heating

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(5) G. R. Schultze, *Oel-Kohle-Erdoel-Teer*, **14**, 113 (1938).

(6) O. Kruber and W. Schade, *Brennstoff-Chem.*, **14**, 124 (1933).

(7) S. F. Birch and W. D. Scott, *Ind. Eng. Chem.*, **24**, 49 (1932).

(8) A. Etart and P. Lambert, *Compt. rend.*, **112**, 945 (1891).

(9) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **68**, 8 (1946).

(10) S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

(11) K. Alder and G. Stein, *Ann.*, **485**, 223 (1931).

(12) Kramer and Spilker, *Ber.*, **29**, 588 (1896).

(13) H. Wieland *Ann.*, **446**, 20 (1925).

(14) H. Staudinger, *Helv. Chim. Acta*, **7**, 27 (1924).

(15) H. Wieland, *Ann.*, **446**, 25 (1926).

(16) H. Staudinger and A. Rheiner, *Helv. Chim. Acta*, **7**, 8, 23 (1924).

(17) H. Staudinger and H. A. Bruson, *Ann.*, **447**, 97 (1926).

(18) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945).

(19) P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

(20) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 1178 (1945).

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TABLE I

CATALYSIS OF 4-CHLOROBENZENETHIOL ADDITION TO *endo*-DICYCLOPENTADIENE AND ALDRIN[a]

Diolefin	Catalyst	Mercaptan Number[b]
None	None	960
Dicyclopentadiene	None	250
Dicyclopentadiene	*t*-Butyl hydroperoxide[c]	190
Dicyclopentadiene	U.V. light[d]	8
Dicyclopentadiene	Air[e]	0[f]
Aldrin	None	272
Aldrin	*t*-Butyl hydroperoxide[c]	8
Aldrin	U.V. light[d]	0
Aldrin	Air[e]	0

[a] *n*-Heptane solutions containing the thiol and one of the two diolefins, both in 0.3 mole/liter concentration, were stored for three hours.[b] The mercaptan numbers (mg. SH sulfur/100 ml.) were determined by potentiometric titration with silver nitrate. [c] 0.001 mole/l. [d] 5 cm. distance. [e] Introduced through a sintered glass inductor. [f] In 2 hr.

the *endo* form in a closed vessel above 100°, conversion occurs to the *exo* form with other side reactions.[23] On the addition of acids,[10,18,19] alcohols, phenols,[20] and water[17] to *endo*-dicyclopentadiene, the *exo* derivatives of dihydrodicyclopentadiene were obtained by an ionic mechanism proposed by Meerwein.[24] Rearrangements were also observed at similar additions to norbornene.[25] However, the radical addition of *p*-toluenethiol to norbornene yielded solely the *exo*-thio ether without rearrangement.[10]

In this laboratory, *endo*-dicyclopentadiene (I) has been converted to the *exo* isomer (III) by hydrogen iodide addition and subsequent dehydroiodination of the *exo*-dihydrodicyclopentadiene derivative (II) by a modified method of Bartlett and Goldstein.[26] The product obtained in this manner had an infrared spectrum different from the *endo* form (Table III). *exo*-Dicyclopentadiene is known to give *exo* derivatives on the addition of both phenylazide and hydrochloric acid.[11,12] Therefore, it was assumed in this laboratory that 4-chlorobenzenethiol addition to *exo*-dicyclopentadiene will give 4-chlorophenylmercaptodihydro-*exo*-dicyclopentadiene (V). It was found that an equimolar amount of 4-chlorobenzenethiol adds to *exo*-dicyclopentadiene with even greater ease than to *endo*-dicyclopentadiene. The reaction yielded an almost colorless liquid sulfide which could be distilled *in vacuo*. This sulfide was not identical with the addition product of the *endo* form. The two sulfides (IV and V) had the same elemental composition and boiling point, but different refractive indices and infrared spectra (Tables II and III). It is felt that these differences indicate that the addition of 4-chlorobenzenethiol to *endo*-dicyclopentadiene does not involve an ionic mechanism and consequently, there is no stereoisomerization to the exo form. As it was indicated earlier by peroxide and ultraviolet catalysis, the reaction takes place according to a radical mechanism.

An even more convincing proof of the *endo* and *exo* structure of the two 4-chlorophenylmercaptodihydrodicyclopentadienes was obtained by oxidizing them to the sulfones (VI and VII). The oxidations were carried out by using hydrogen peroxide in acetic anhydride–acetic acid media at about 50°. It is interesting to note that, under such conditions, the oxidation was somewhat selective to the sulfide group and did not affect the cyclopentene group in the molecule. The 4-chlorophenylsulfonyldihydrodicyclopentadienes (VI and VII) obtained had different infrared spectra (Table III), different melting points (Table II), and gave a definite melting point depression on mixing. These oxidation products had no monohydric alcohol or vicinal glycol content according to the esterification method[27] and periodic acid method,[28] respectively. It is also noted that there were no epoxide groups in the above compounds as is shown by the absence of the characteristic absorption at 11.78 microns.[29,30] A similar selective oxidation of an unsaturated sulfide, 3-chloro-*exo*-norbornen-2-yl *p*-tolyl sulfide, to the corresponding sulfones was carried out by Cristol and co-workers.[29]

On the basis of these results, it is concluded that the addition of 4-chlorobenzenethiol to dicyclopentadiene normally proceeds by a radical mechanism, and that the resulting sulfides (IV, V) can be oxidized to the corresponding sulfones (VI, VII). Consequently, the reactions examined can be summarized by the equations that follow next.

2. *Aldrin-4-chlorobenzenethiol.* Aldrin, *endo-exo*-1,2,3,4,10,10 - hexachloro - 1,4,4a,5,8,8a - hexahydro - 1,4,5,8 - dimethanonaphthalene (VIII) was selected for our studies as a diolefin having a highly reactive bicycloheptene group and a relatively unreactive chlorinated bicycloheptene group. These differences in the reactivities of the double

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(24) H. Meerwein and K. van Emster, *Ber.*, **53B,** 1815 (1920).

(25) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76,** 4072 (1954).

(26) P. D. Bartlett and I. S. Goldstein, *J. Am. Chem. Soc.*, **69,** 2553 (1947).

(27) C. L. Ogg, W. L. Porter, and C. O. Willits, *Ind. Eng. Chem., Anal. Ed.*, **17,** 394 (1945).

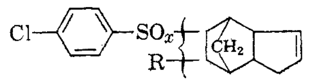
(28) *Organic Analysis* (Ed. Board: J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, A. Weissberger) Vol. I, *Determination of Hydroxyl Groups* (V. C. Mehlenbacher) Interscience Publishers Inc., New York, 1953, p. 45.

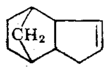
(29) S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *J. Am. Chem. Soc.*, **79,** 6035 (1957).

(30) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75,** 1175 (1953).

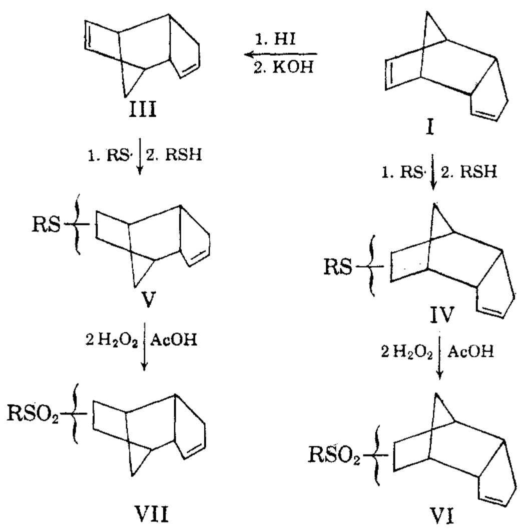
TABLE II

PRODUCTS OF 4-CHLOROBENZENETHIOL-DICYCLOPENTADIENE ADDITION AND CO-OXIDATION



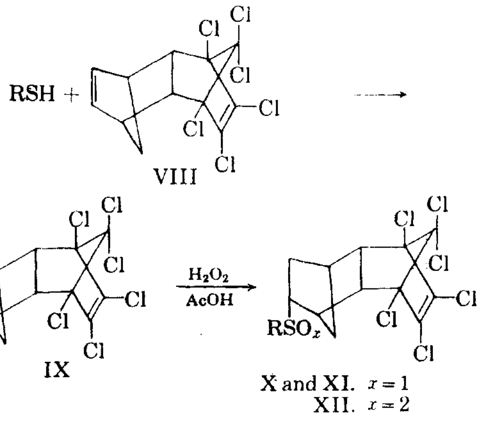
No.	x	R		Formula	Yield, %	M.P.,[a] (n_D^{20})	Calcd., % C	Calcd., % H	Calcd., % Cl	Found, % C	Found, % H	Found, % Cl
IV	0	H	*endo*	$C_{16}H_{17}ClS$	94.5	(1.6073)	69.42	6.19	12.81	69.39	6.14	12.5
V	0	H	*exo*		96	(1.6053)				69.30	6.31	12.6
VI	2	H	*endo*	$C_{16}H_{17}ClO_2S$	55	113–114.5	62.23	5.55	11.48	62.31	5.75	11.4
VII	2	H	*exo*		87	84–85				61.87	5.76	11.2
XIV	1	OH	*endo*	$C_{16}H_{17}ClO_2S$	50	218–220	62.23	5.55	11.48	62.37	5.58	11.3
XV	1	OH	*endo*		50[b]	182–184				61.92	5.53	11.3
XVII	1	OH	*exo*		11	167–168				62.32	5.76	11.5

[a] Uncorrected. [b] Total yield of the mixture of the two isomers.



bonds are shown by selective addition of halogens[31] and hydrogen halides[32] to the unchlorinated double bond, and by the selective oxidation[33] and sulfuration[31] of this bond. In such selective reactions, Aldrin, which is an important insecticide,[34,35] yielded a number of further good insecticides, *e.g.*, Dieldrin by epoxidation [33,35] Cristol and Arganbright[36] found that an equimolar amount of 4-toluenethiol readily adds to 6-chloro-Aldrin to yield *exo* - 2 - *p* - tolylmercapto - *endo* - 3,5,6,7,8,9,9-heptachloro - *exo* - endo - 1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8 - dimethanonaphthalene. It was of interest to know whether or not radical type addition of 4-chlorobenzenethiol to Aldrin is also limited to the unchlorinated double bond. At first, the addition of 4-chlorobenzenethiol to Aldrin (VIII) was examined.

It was found that an equimolar amount of 4-chlorobenzenethiol readily adds to Aldrin in a spontaneous exothermic reaction to yield a colorless crystalline sulfide (IX). The reaction can be catalyzed by a peroxide or ultraviolet light (Table I). Therefore, it is assumed that *cis-exo* addition takes place according to a radical mechanism, as in the case of 4-toluenethiol and chloro-Aldrin. A second molecule of 4-chlorobenzenethiol could not be added to the Aldrin molecule without catalysis. This indicates the unreactivity of the chlorinated double bond of Aldrin, which was expected on the basis of the literature cited above. The relative unreactivity of the chlorinated double bond was also shown by oxidizing with hydrogen peroxide in acetic anhydride–acetic acid media the sulfide addition product to the isomeric sulfoxides (X and XI) and to the sulfone (XII), without attacking the double bond:



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[31] S. B. Soloway, U.S. Patent 2,676,131.

[32] R. E. Lidov and H. Bluestone, U.S. Patent 2,714,-617.

[33] R. E. Lidov and S. B. Soloway, Brit. Patent 692,544.

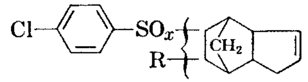
[34] C. W. Kearns, C. J. Weinman, and G. C. Decker, *J. Econ. Entomol.*, **42**, 127 (1949).

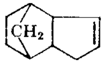
[35] R. E. Lidov, U.S. Patent 2,635,979.

[36] S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 6039 (1957).

TABLE III

Infrared Absorption Peaks of 4-Chlorobenzenethiol-Dicyclopentadiene Addition and Co-oxidation



No.	x	R		Absorption Peaks (μ: s Very Strong; m, Medium; w, Weak)
I[a]	*endo*-Dicyclopentadiene			3.25s, 3.45s 6.94s 7.48s 8.02s 8.86m, 9.15w 9.80m, 10.1m 10.68m, 10.92s 11.05s, 12.45s, 14.24s
III[a]	*exo*-Dicyclopentadiene			3.25s, 3.45s 6.94s 7.38, 7.45, 7.55 8.02s 8.86w, 9.14m 9.6m, 9.9s 10.1w 10.60s, 10.92m 11.05s, 12.53vs 14.24vs
IV[a]	0	H	*endo*	3.25s, 3.35vs 6.78vs 7.2s, 7.38s, 7.82s 7.89s, 8.14w 9.15vs 9.52w, 9.90vs 10.6s 10.88w 11.87w 14.55vs
V[a]	0	H	*exo*	3.25s, 3.43vs 6.78vs 7.2s, 7.38s, 7.82w, 7.89w 9.15vs 9.90vs 10.6s 12.63 14.40vs
VI[b]	2	H	*endo*	3.4m 6.3vs, 6.80s, 6.87s 6.94m, 7.2s, 7.39m, 7.65vs 8.78vs, 9.23vs 9.89vs 10.57m 11.1s
VII[b]	2	H	*exo*	3.47s 6.3vs, 6.84s 6.94s, 7.2s, 7.39s, 7.75vs 8.85vs, 9.28vs 9.93s 10.56s 11.04s
XIII[b]	0	O_2H	*endo*	2.98m, 3.38s 6.35w, 6.79s, 6.85w, 6.9w 7.21m, 7.4w, 7.73w, 7.9w 8.74w, 8.92w, 9.17vs, 9.29s 9.56vs, 9.93vs 10.65w, 11.07w
XIV[b]	1	OH	*endo*	2.95s, 3.36s 6.25m, 6.77s, 6.82m, 6.9m 7.19s, 7.48m, 7.75s, 7.89s 8.75m, 8.81m, 9.17vs, 9.28vs 9.55vs, 9.72vs 10.57s, 11.08m
XV[b]	1	OH	*endo*	2.99s, 3.41s 6.25m, 6.78s, 6.81s, 6.9m 7.21m, 7.45m. 7.65s, 7.91m 8.66m, 8.93m, 9.18vs, 9.3vs 9.57vs, 9.75vs 10.56m, 11.06m
XVII	1	OH	*exo*	2.9s, 3.34s 6.28m, 6.73vs, 6.82s, 6.89m 7.16s, 7.46w 7.71w, 7.92m 8.76m, 8.93w, 9.15vs, 9.26vs 9.55vs, 9.7vs, 9.9vs 10.54w, 11.08w

[a] Without solvent. [b] In chloroform solution.

Some physical and analytical data and characteristic absorption spectra of these oxidation products are shown in Table IV and Table V, respectively. The analytical data agree well with the sulfoxide and sulfone structures. Neither of the compounds had any monohydric alcohol or vicinal glycol content. The characteristic epoxide absorption at 11.78 μ[29,30] was absent.

B. Co-oxidation. 1. *Dicyclopentadiene-4-chlorobenzenethiol.* Dumanois and co-workers reported[37] that *endo*-dicyclopentadiene alone is resistant to oxidation in air below 300° and acts as an inhibitor for the combustion of more easily oxidizable hydrocarbons, such as decahydronaphthalene. At ambient temperatures, 4-chlorobenzenethiol is also resistant to air oxidation.

It was first reported by Kharasch and co-workers[38] that hydrocarbon solutions containing both a reactive olefin (styrene) and a mercaptan are readily co-oxidized by molecular oxygen at room temperature. In the case of styrene, Kharasch has proved that such an oxidation is initiated by the formation of mercapto radicals and leads to substituted hydroxyethyl sulfoxides. Ford, Pitkethly, and Young[39] indicated the formation of an unstable hydroperoxide intermediate in benzene solution during the co-oxidation of benzenethiol and indene by oxygen. Such hydroperoxide intermediates from the co-oxidation of thiols with styrenes and indene were isolated by Oswald.[1a,2] These investigations proved that the reaction proceeds with the following mechanism:

$$R{-}S\cdot + CHR'{=}CR_2'' \longrightarrow R{-}S{-}CHR'{-}CR_2''\cdot$$

$$R{-}S{-}CHR'{-}CR_2''\cdot + O_2 \longrightarrow R{-}S{-}CHR'{-}CR_2''{-}O_2\cdot$$

$$R{-}S{-}CHR'{-}CR_2''{-}O_2\cdot + RSH \longrightarrow R{-}S{-}CHR'{-}CR_2''{-}O_2H(+RS\cdot)$$

As expected on the basis of the above studies of mercaptan–monoolefin co-oxidation, *n*-heptane solutions, containing both *endo*-dicyclopentadiene and 4-chlorobenzenethiol in equimolar amounts, were readily oxidized by air at ambient temperatures (Table I). After one-half hour of aeration, a sirup separated, which had 12% of the peroxide content calculated for *p*-chlorophenylmercaptohydroperoxydihydro-*endo*-dicyclopentadiene. This oily intermediate solidified on standing and lost most of its peroxide content. On recrystallization, two isomeric crystalline alcohols (Compounds XIV and XV in Tables II and III) were obtained. On concentrating the *n*-heptane phase, the same isomers (XIV and XV) were obtained together with some of the sulfide addition product (IV).

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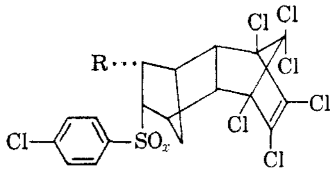
(37) P. Dumanois, G. Rentenauer, and M. Prettre, *Compt. rend.*, **208**, 1814 (1939).

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

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

TABLE IV

PRODUCTS OF 4-CHLOROBENZENETHIOL-ALDRIN ADDITION AND CO-OXIDATION



No.	*x*	R	Formula	Yield, %	M.P.	Calcd., % C	Calcd., % H	Calcd., % Cl	Found, % C	Found, % H	Found, % Cl
IX	0	H	$C_{18}H_{13}Cl_7S$	73	106.5–108.5	42.43	2.57	48.71	42.21	2.73	48.4
X	1	H	$C_{18}H_{13}Cl_7OS$	36	206–208.5	41.13	2.49	47.23	40.99	2.57	47.2
XI	1	H		30	190–193				40.92	2.48	47.0
XII	2	H	$C_{18}H_{13}Cl_7O_2S$	84	223–226	39.92	2.42	45.83	39.92	2.57	46.0
XVIII	0	O_2H	$C_{18}H_{13}Cl_7O_2S$	15.4	116–119	39.92	2.42	45.83	40.62	2.81	45.2
XIX	1	OH	$C_{18}H_{13}Cl_7O_2S$	35.8	248–249.5	39.92	2.42	45.83	39.98	2.49	45.8
XX	1	OH		20.3	207–210				40.23	2.60	45.9

The change of the peroxidic intermediate was also followed by the change of its infrared spectrum with time in chloroform solution. A comparison of the spectra taken at different time intervals shows an increase with time in absorption at 3 μ, of a characteristic absorption peak for the hydroxyl group.

The co-oxidation of *endo*-dicyclopentadiene and 4-chlorobenzenethiol by molecular oxygen could be also carried out at lower temperatures. At about −5° ultraviolet light was an effective initiator of the reaction. The reaction was practically complete in an hour. An intermediate having 40% of the calculated peroxide content of the hydroperoxide co-oxidation product (XIII) was isolated from the reaction mixture. This intermediate was an unstable, colorless, viscous liquid at room temperature and yielded the two isomeric crystalline alcohols (XIV, XV) on rearrangement. An infrared study of this rearrangement in chloroform showed that besides the alcohols some carbonyl compound is also formed.

Equimolar amounts of *exo*-dicyclopentadiene and 4-chlorobenzenethiol were also readily co-oxidized in *n*-heptane solution in a similar manner. On air oxidation at room temperature, a peroxidic, viscous liquid intermediate precipitated from the solution in two hours. On standing overnight, this liquid turned to a semisolid which yielded a crystalline alcohol (XVII). The latter compound had the same composition as the alcohols derived from the *endo*-dicyclopentadiene-4-chlorothiophenol co-oxidation (XIV, XV, see Table II for data), but different infrared spectrum (Table III) and melting point.

When a *n*-heptane solution containing the *exo*-dicyclopentadiene and 4-chlorobenzenethiol was oxygenated at −5° under ultraviolet irradiation, a hydroperoxide with 43% of the active oxygen content of the co-oxidation intermediate (XVI) was isolated. This intermediate was also an unstable, colorless, viscous liquid at room temperature. Infrared spectra of a chloroform solution of this liquid intermediate showed that hydroxyl and carbonyl groups are formed slowly and spontaneously.

When the reaction mixture contained one mole of dicyclopentadiene for two moles of 4-chlorobenzenethiol, one mole of 4-chlorobenzenethiol remained unchanged during the aeration. This showed again that only one double bond of the dicyclopentadiene took part in the reaction. The absence of addition between the crystalline isomeric products and phenylazide indicated that the co-oxidation reaction took place at the double bond of the bicycloheptene part of dicyclopentadiene. On the basis of the addition of 4-chlorobenzenethiol to dicyclopentadiene and of the co-oxidation of monoolefins and mercaptans[1a,2,38,39] and of the observations reported above, it is proposed that the co-oxidation of 4-chlorobenzenethiol and *endo*-dicyclopentadiene follows the reaction route by a radical mechanism, as shown below:

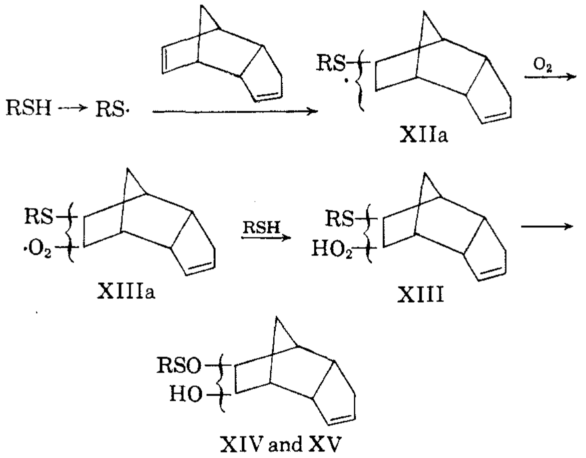
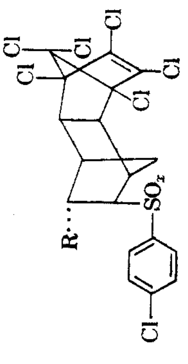


TABLE V. INFRARED ABSORPTION PEAKS OF PRODUCTS OF 4-CHLOROBENZENETHIOL-ALDRIN ADDITION AND CO-OXIDATION



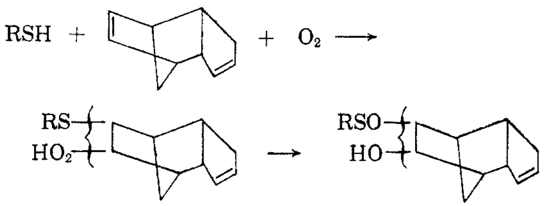
No.	x	R	Absorption Peaks (μ; vs, Very Strong; m, Medium; w, Weak)
VIII[a]	—	— (Aldrin)	3.36m, 3.42w 6.22vs 7.61vs, 7.85m, 8.04m 9.02s, 9.12s, 9.22s, 9.39s 9.73vs, 9.85s 9.99s, 10.99s, 11.16vs, 11.28vs
IX[a]	0	H	3.39s 6.25vs, 6.35s 7.20s, 7.47m, 7.70m, 7.75s, 7.90s 8.76m, 9.05s, 9.18s, 9.32s 9.90s 10.53s, 11.0s, 11.25s
X[a]	1	H	2.9m[c], 3.38m 6.25s, 6.30s 7.18s, 7.56s, 7.68s, 7.75s, 7.89s 8.74s, 9.02vs, 9.2vs, 9.32s 9.9vs 10.47s 11.33s
XI[a]	1	H	2.9m[c], 3.38m 6.25s, 6.35s 7.18s, 7.46s, 7.67s, 7.75s, 7.89s 8.77m, 9.02vs, 9.2vs, 9.32vs 9.9vs 10.47s, 10.98vs, 11.33s
XII[a]	2	H	2.83m[c], 3.38m 6.25vs, 6.30vs 7.18s, 7.58vs, 7.70vs, 7.75s, 7.88vs 8.75vs, 9.04s, 9.25vs, 9.32s 9.88s 10.45m, 11.0s, 11.3s
XVIII[b]	0	O_2H	3.33s 6.24s, 6.31 7.34vs, 7.63s 8.67m, 9.05m, 9.16m, 9.34s 9.74vs 11.06m
XIX[a]	1	OH	3.05s, 3.35w 6.25s 6.35w 7.2w, 7.55w, 7.75w, 7.9m 9.01s, 9.18vs, 9.30s 9.92vs 10.6w, 11.0m, 11.2w
XX[a]	1	OH	2.79s, 3.0s, 3.42 6.25s, 6.35w 7.2m, 7.52w 7.9s 8.92s, 9.17s, 9.30vs 9.92s 10.55w, 10.98w, 11.29m

[a] In chloroform solution. [b] In carbon tetrachloride solution. [c] The compound has no monohydric alcohol or vicinal glycol content according to the esterification method[27] and periodic method[28], respectively. The characteristic epoxide absorption at 11.78 μ[29, 30] is also absent.

It is proposed that the first relatively stable product of the co-oxidation reaction is the hydroperoxide (XIII). From the hydroperoxide, the hydroxyethyl sulfoxide isomers (XIV and XV) are obtained by rearrangement. The latter are completely stable at ambient temperatures, but decompose on melting. Some of the substituted mercaptoethyl radicals (XIIa), especially if the oxygen concentration is low, abstract a hydrogen from another molecule of mercaptan to yield the sulfide (IV) by-product.

The proposed structure of these hydroxysulfoxides is supported by elemental analyses and infrared spectra. Investigations of mercaptan–monoolefin co-oxidations[1a, 2, 38, 39] also point to these structures by analogy. The stereochemistry of these 4-chlorophenylsulfinylhydroxydihydro-*endo*-dicyclopentadienes was, however, not examined.

The proposed mechanism for the co-oxidation of *exo*-dicyclopentadiene and 4-chlorobenzenethiol is the same. The reaction can be illustrated by the following summarized equation:

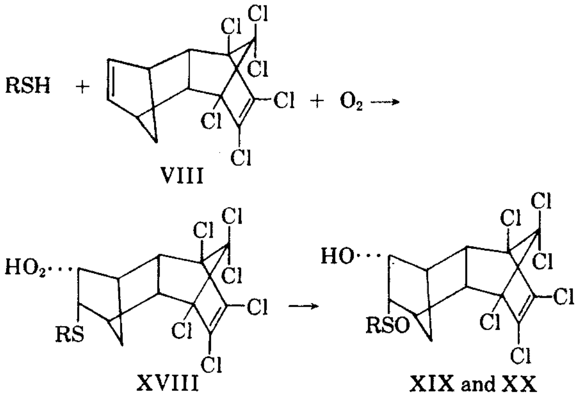


XVI XVII

On the basis of these results, it is concluded that peroxides containing sulfur, which are formed readily by co-oxidation of dicyclopentadiene and aromatic mercaptans with air, may be responsible for the instability of petroleum distillates containing these components.

2. *Aldrin and 4-chlorobenzenethiol.* In the co-oxidation of 4-chlorobenzenethiol-dicyclopentadienes, the hydroperoxide intermediates were indicated, but could not be isolated in a pure state because they were unstable liquids. It was thought that the co-oxidation of 4-chlorobenzenethiol with a higher molecular weight diolefin, such as Aldrin (VIII) would more likely give a solid, crystalline hydroperoxide intermediate. Equimolar amounts of chlorobenzenethiol and Aldrin were readily co-oxidized by air at ambient temperatures (Table I). Also, the co-oxidation could be catalyzed by ultraviolet light irradiation. When an *n*-heptane solution was aerated at 0° and irradiated with ultraviolet light, the precipitation of a solid, crystalline hydroperoxide co-oxidation product started in five minutes. After twenty-five minutes, this hydroperoxide was removed from the reaction mixture by filtration. It was found to have 90% of the peroxide content calculated for *exo*-2-*p*-chlorophenylmercapto-3-hydroperoxy-*endo*-5,-6,7,8,9,9-hexachloro-*exdo*-*eno*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XVIII).

However, the proposed hydroperoxide structure (XVIII) is not supported by the infrared spectrum which shows no definite hydroxyl absorption at 3 μ (Table V). When a chloroform solution of this hydroperoxide was left to stand for five days, the solution lost its peroxide content and crystals precipitated from it. These crystals were identical to one of the isomeric products (XIX) obtained by the recrystallization of the products formed by further air introduction into the *n*-heptane reaction mixture. Both of these isomers (XIX and XX) show infrared absorption peaks at 3 μ (Table V). Their elemental composition corresponds to the values calculated for *exo*-2-*p*-chlorophenylsulfinyl-3-hydroxy - *endo* - 5,6,7,8,9,9 - hexachloro - *exo* - *endo*-1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8 - dimethanonaphthalene (Table IV) which would result by a rearrangement analogous to those observed in earlier studies of monoolefin-mercaptan co-oxidations.[1a,2,39] Consequently, it is proposed that the co-oxidation of 4-chlorobenzenethiol–Aldrin proceeds by a radical mechanism as it was proposed for 4-chlorobenzenethiol–dicyclopentadiene co-oxidation. The first stable product of the co-oxidation is the sulfur-containing hydroperoxide (XVIII) which rearranges to the substituted 4-chlorophenylsulfinylethanol isomers (XIX and XX).



In conclusion, one double bond of nonconjugated diolefins having an unsubstituted reactive bicyclo-[2.2.1]heptene group can be readily co-oxidized to yield unstable mercaptoethyl hydroperoxides containing a less reactive double bond. These hydroperoxides rearrange to the corresponding sulfinylethyl alcohols.

EXPERIMENTAL

Materials. 4-Chlorobenzenethiol was recrystallized from *n*-heptane before use and had a m.p. of 52–53°. Dicyclopentadiene was freshly distilled under nitrogen. *t*-Butyl hydroperoxide was used as supplied by the Wallace and Tiernan Corp.

Technical Aldrin (VIII) was recrystallized from *n*-heptane and then from methanol. The purified compound, *endo-exo*-1,2,3,4,10,10 - hexachloro - 1,4,4a,5,8,8a - hexahydro-1,4,5,8-dimethanonaphthalene had a melting point of 101–102°. A chloroform solution of the compound had the absorption peaks listed in Table V.

The solvents used were all C.P. Reagents.

The addition of 4-chlorobenzenethiol to endo-dicyclopentadiene. In the absence of catalyst without solvent. About 13.2 g. (0.1 mole) of *endo*-dicyclopentadiene (I) was added to 14.5 g. (0.1 mole) of 4-chlorobenzenethiol under nitrogen. An immediate dissolution of the chlorobenzenethiol and a rise of the temperature of the reaction mixture were observed. The reaction mixture was cooled by water to keep the temperature below 70°, and kept under nitrogen by bubbling nitrogen into it. After coming to room temperature, the yellow liquid reaction mixture was allowed to stand for 4 days to complete the addition. Then the mixture was distilled *in vacuo.* Between 145–146° at 2 mm., 26.2 g. (94.5%) of 4-chlorophenylmercaptodihydro-*endo*-dicyclopentadiene (IV) was obtained as a light yellow liquid.

With solvent. A solution of 13.2 g. (0.1 mole) of *endo*-dicyclopentadiene and 14.5 g. (0.1 mole) of 4-chlorobenzenethiol, each in 0.3 mole/l. concentration, in *n*-heptane was prepared under nitrogen. The solution was left to stand under nitrogen for a week to complete the addition of the thiol. Then the *n*-heptane was removed by distillation. The residue was fractionated *in vacuo* to yield 25.5 g. (92%) of 4-chlorophenylmercaptodihydro-*endo*-dicyclopentadiene (IV).

With hydroperoxide initiator. About 0.09 g. (0.001 mole) of *t*-butyl hydroperoxide was added to the *n*-heptane solution described above. Then the reaction mixture was left to stand for 1 week and worked up as before. 4-Chlorophenylmercaptodihydro-*endo*-dicyclopentadiene (IV) was obtained in 93% yield.

In the presence of an excess of 4-chlorobenzenethiol. A solution of 13.2 g. (0.1 mole) of *endo*-dicyclopentadiene and 29 g. (0.2 mole) of 4-chlorobenzenethiol in *n*-heptane was prepared. The concentration of the solution for the two compounds was 0.3 mole/l. and 0.6 mole/l., respectively. After standing for 1 week at room temperature, the reaction mixture was worked up as above. After the sublimation of the excess chlorothiophenol *in vacuo,* 23.5 g. (85%) 4-chlorophenylmercaptodihydro - *endo* - dicyclopentadiene (IV) was obtained.

The 4-chlorophenylmercaptodihydro-*endo*-dicyclopentadiene products obtained in these experiments were identified by boiling point, refractive index (n_D^{20}), and infrared spectra. Data on the purified product (IV) are given in Tables II and III.

Hydroiodination of endo-dicyclopentadiene with an excess of azeotropic aqueous hydrogen iodide. A heterogeneous mixture of 56 g. (0.5 mole) of dicyclopentadiene and 224.5 g. of 57% aqueous hydrogen iodide (1 mole of hydrogen iodide) was effectively stirred under nitrogen for 12 hr. An exothermic reaction took place. By use of occasional water cooling, the temperature of the reaction mixture was not allowed to rise above 50°. When the reaction was carried out in this manner, a reddish organic phase resulted. This was dissolved in ether, washed with water in the presence of small amount of alcohol (to avoid stable emulsion) and distilled in nitrogen atmosphere. Working in this manner, 116 g. (67%) of iododihydro-*exo*-dicyclopentadiene b.p. 80–81°/2 mm. was obtained. The original method of Bartlett and Goldstein[26] gave a 44% yield.

Dehydroiodination of iododihydro-exo-dicyclopentadiene. A stirred mixture of 129.5 g. (0.05 mole) of iododihydro-*exo*-dicyclopentadiene and a solution of 67.2 g. (1.2 mole) of potassium hydroxide in 250 ml. of 95% aqueous ethyl alcohol was refluxed for 4 hr. under nitrogen atmosphere. Then the mixture was diluted with water and extracted with ether. The ether phase was washed with water, dried, and distilled to yield crude *exo*-dicyclopentadiene and 35 g. of distillation residue. On redistilling the crude product, 40 g. (60.5%) of *exo*-dicyclopentadiene (III), n_D^{20} 1.5105, was obtained between 49–50° at 8 mm.

Some characteristic infrared absorption peaks of the *exo* and *endo* forms of dicyclopentadiene are compared in Table III.

Addition of 4-chlorobenzenethiol to exo-dicyclopentadiene. The addition of 14.5 g. (0.1 mole) of 4-chlorobenzenethiol, 13.2 g. (0.1 mole) of *exo*-dicyclopentadiene (III) and *endo*-dicyclopentadiene in the absence of solvent was carried out in the same manner. The *exo*-dicyclopentadiene reacted even more exothermically with 4-chlorobenzenethiol. The reaction mixture yielded on vacuum distillation 26.5 g. (96%) of an almost colorless liquid, 4-chlorophenylmercaptodihydro-*exo*-dicyclopentadiene (V) at 146–147°/2 mm. Some physical properties and analytical data are compared with those of the *endo* derivative in Tables II and III.

The oxidation of 4-chlorophenylmercaptodihydro-endo-dicyclopentadiene. To a solution of 13.8 g. (0.05 mole) of 4-chlorophenylmercaptodihydro-*endo*-dicyclopentadiene (IV) in a mixture of 40 ml. of acetic anhydride and 15 ml. of acetic acid, 11.2 g. (0.1 mole) of 30% aqueous hydrogen peroxide was added by increments with shaking during 20 min. The temperature was kept at about 50° with frequent cold water cooling. When the reaction mixture ceased to be exothermic, it was left to stand at room temperature for 24 hr. Then water was added to the clear colorless mixture until it became turbid. On concentrating, a crude crystalline product precipitated out of the solution. It was removed by filtration and recrystallized from methanol to yield 8.5 g. (55%) of 4-chlorophenylsulfonyldihydro-*endo*-dicyclopentadiene (VI) as colorless crystals melting between 112–114°. Some analytical data of the compound are shown in Table II.

In another experiment, 14.5 g. (0.1 mole) of 4-chlorobenzenethiol and 14.5 g. (0.11 mole) of *endo*-dicyclopentadiene were mixed to produce the adduct. The crude adduct was then dissolved in 200 ml. of glacial acetic acid and oxidized by slowly adding 22.4 g. (0.2 mole) of hydrogen peroxide with shaking at 40°. By precipitation with water and recrystallization from methanol 27.8 g. (90%) 4-chlorophenylsulfonyldihydro-*endo*-dicyclopentadiene, identical with the above product was obtained.

The oxidation of 4-chlorophenylmercaptodihydro-exo-dicyclopentadiene. 4-Chlorophenylmercaptodihydro-*exo*-dicyclopendadiene (V) was oxidized in the same manner as the *endo* derivative above. 4-Chlorophenylsulfonyldihydro-*exo*-dicyclopentadiene (VII) was obtained as white platy crystals of m.p. 84–85° in 57% yield. Some physical and analytical data of the compound are compared with the corresponding *endo* derivative in Tables II and III.

In another experiment, the oxidation of 27.7 g. (0.1 mole) of 4-chlorophenylmercaptodihydro-*exo*-dicyclopentadiene was carried out in 200 ml. of acetic acid with 22.4 g. (0.2 mole) of hydrogen peroxide to yield 19.7 g. (70%) of the sulfone (VII).

The addition of 4-chlorobenzenethiol to Aldrin. In the absence of catalysts. *n*-Heptane solutions of 2.9 g. (0.02 mole) of 4-chlorobenzenethiol and 7.3 g. (0.02 mole) of Aldrin (VII) were prepared and mixed under nitrogen to give a solution of 0.3 mole/l. concentration for both reagents. The mixture was left to stand closed from air at room temperature for a week to complete the addition reaction. Then most of the *n*-heptane was evaporated. The crude crystalline product was removed by filtration and recrystallized from ethanol. In this manner, 7.5 g. (73%) of *exo*-2-*p*-chlorophenylmercapto-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (IX), m.p. 106.5–108.5°, was obtained as fine colorless needles. Analytical and physical data are shown in Tables IV and V.

In the presence of ultraviolet light. An *n*-heptane solution (66 ml.) of the reagents, prepared as described above, was irradiated in a Vycor (96% quartz) flask by an ultraviolet lamp (250 v., 100 w, 60 cy.; G.E. 9T64Y20) from 5-cm. distance, while nitrogen was bubbled into it. After 1 hr., the reaction mixture was concentrated by an air stream, while the walls were scratched from time to time to initiate the crystallization of the product. This product was recrystallized from ethanol to yield 8.5 g. (83%) of *exo*-2-*p*-chlorophenylmercapto-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (IX), identical with the product of uncatalyzed addition.

The oxidation of exo-2-p-chlorophenylmercapto-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene. To the sulfoxide. To a solution of 5.1 g. (0.01 mole) of the sulfide in 40 ml. of 1:1 acetic acid–acetic anhydride, 0.34 g. (0.01 mole) hydrogen peroxide was added in the form of an aqueous 30% solution at 40°. After the addition, the mixture was kept for 2 hr. at that temperature, and then left to stand overnight at room temperature. The following day, the mixture was concentrated to yield the crude product as a crystalline precipitate. This was removed by filtration, recrystallized several times from toluene to yield the isomeric sulfoxides of m.p. 206–208.5° (X) and 190–193° (XI) as fine colorless needles in 36% (1.9 g.) and 30% (1.6 g.) yield. Some physical and analytical data of these compounds (*exo*-2-*p*-chlorophenylsulfinyl-*endo*-5,6,7,8,-9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalenes, (X and XI), are shown in Tables IV and V.

To the sulfone. When a solution of 5.1 g. (0.01 mole) of the sulfide (IX) was oxidized with 0.68 g. (0.02 mole) of hydrogen peroxide as 30% aqueous solution as described above, a crystalline slurry resulted. This was filtered. Recrystallization of the raw crystalline product from toluene-methanol yielded 4.5 g. (84%) *exo*-2-*p*-chlorophenylsulfonyl-*endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XII), m.p. 223–226°. Analytical data and characteristic absorption peaks of the compounds are shown in Tables IV and V, respectively.

Co-oxidation of endo-dicyclopentadiene and 4-chlorobenzenethiol. At room temperature. A heptane solution (320 ml.) of 14.5 g. (0.1 mole) of 4-chlorobenzenethiol was prepared and placed into a 500-ml. measuring cylinder. Air introduction through a sintered glass inductor of 7.5 cm.^{2} sintered area was started into the mixture and then 13.2 g. (0.1 mole) of *endo*-dicyclopentadiene was added to it. The air introduction was continued for 2 hr. at room temperature. After 0.5 hr., a colorless liquid started to precipitate. This bottom liquid phase became white and turbid after an additional 0.5 hr. After a total of 2 hr. of air introduction, no mercaptan was left unconverted in the reaction mixture and the bottom phase had turned to a white crystalline solid. Altogether, 7 g. (50%) of crystalline *p*-chlorophenylsulfinylhydroxy-*endo*-dihydrodicyclopentadiene isomer mixture was removed from the mixture by filtration. By several recrystallizations from toluene-*n*-heptane, two hydroxyethyl sulfoxide isomers of m.p. 218–220° (XIV) and 182–184° (XV) were separated. Their analytical data and infrared spectra are shown in Tables II and III, respectively.

The *n*-heptane filtrate on evaporation left 7 g. of a yellow oil as liquid residue. On vacuum distillation under nitrogen, this yielded 5 g. (35.7%) of *p*-chlorophenylmercaptodihydro-*endo*-dicyclopentadiene between 144–154° at 2 mm. This was converted to *p*-chlorophenylsulfonyldihydro-*endo*-dicyclopentadiene by oxidation with hydrogen peroxide in acetic acid–acetic anhydride medium in a manner described earlier. It gave no melting point depression with the sulfone prepared from the pure sulfide.

At −5°. Oxygen was introduced at −5° into a 160-ml. *n*-heptane solution of 3.6 g. (0.025 mole) of 4-chlorobenzenethiol and 3.3 g. (0.025 mole) of *endo*-dicyclopentadiene contained in a Vycor flask. After 1 hr. of oxygenation under ultraviolet with a 250 v., 100 w., 60 cycle lamp from a distance of 10 cm., the concentration of the free mercaptan was less than 1% of the original. (In a control experiment without irradiation, only 75% of the mercaptan was converted.) By the end of the 1-hr. reaction period, a white semisolid peroxidic precipitate was formed. When the mother liquor was decanted and cooled in a Dry Ice–acetone bath, white crystals precipitated. These were filtered off and washed with cold *n*-pentane. These crystals melted on coming to room temperature to yield a colorless viscous liquid of n^{20}_D 1.5820. This liquid was analyzed for peroxide by the potassium iodide method.[40] The active oxygen content found was 40% of the value calculated for *p*-chlorophenylmercaptohydroperoxydihydro - *endo* - dicyclopentadiene (XIII).

Anal. Calcd. for $C_{16}H_{17}ClO_2S$: C, 62.23; H, 5.55. Found: C, 62.69; H, 6.03.

The infrared spectrum of the above peroxide intermediate in chloroform solution changed on standing at room temperature. Within an hour, a new absorption peak at 5.77 μ appeared, which is characteristic of the carbonyl group. The hydroxyl absorption at 2.9 μ and the sulfoxy absorption between 9–10 μ became stronger.

From the *n*-heptane filtrate, 1 g. of a white, crystalline solid precipitated overnight. This had 8.5% of the active oxygen content of the assumed hydroperoxide co-oxidation product. This product was still peroxidic after recrystallization from toluene; it started to turn brown at about 140° and melted between 175–185°.

The above peroxidic products were combined and recrystallized several times to yield a total of 4.4 g. (60%) of the *p*-chlorophenylsulfinylhydroxydihydro-*endo*-dicyclopentadiene isomers described in the previous example.

Co-oxidation of exo-dicyclopentadiene and 4-chlorobenzenethiol. At room temperature. About 100 ml. of *n*-heptane solution containing 4.8 g. (0.03 mole) of 4-chlorobenzenethiol and 4.3 g. (0.03 mole) of *exo*-dicyclopentadiene was aerated for 2 hr. By the end of the 2 hr., no free mercaptan was present and a viscous oil precipitated from the reaction mixture. After standing overnight, this oil turned to a semisolid. The supernatant *n*-heptane solution was decanted to leave 4.1 g. of the semisolid. The latter was taken up in 25 ml. of acetone to dissolve the oil. Then the mixture was filtered and the solid was recrystallized from toluene-*n*-heptane to yield 1.1 g. (11%) of colorless, crystalline *p*-chlorophenylsulfinylhydroxydihydro - *exo* - dicyclopentadiene, m.p. 167–168° (XVII). Some analytical data and characteristic absorption peaks of the compound are shown in Tables II and III, respectively.

At −5°. An *n*-heptane solution (160 ml.) of 3.6 g. (0.025 mole) of 4-chlorobenzenethiol and 3.3 g. (0.025 mole) of *exo*-dicyclopentadiene was oxygenated at about −5° under ultraviolet irradiation. The reaction proceeded as in the case of *endo*-dicyclopentadiene and formed a white, semisolid peroxidic precipitate in 1 hr. Further cooling of the liquid part of the reaction mixture in a Dry Ice-acetone bath yielded a crystalline precipitate. The latter had 43% of the peroxide content calculated for *p*-chlorophenylmercaptohydroperoxydihydro - *exo* - dicyclopentadiene (XVI). At room temperature, this product is an unstable liquid of n^{20}_D 1.5850.

Anal. Calcd. for $C_{16}H_{17}ClO_2S$: C, 62.23; H, 5.55. Found: C, 62.38; H, 5.95.

Co-oxidation of 4-chlorobenzenethiol and Aldrin. Separation of the stable products. Into 333 ml. of *n*-heptane solution containing 7.23 g. (0.05 mole) of 4-chlorobenzenethiol and 18.25 g. (0.05 mole) of Aldrin (VIII), air was introduced for 3 hr. at room temperature. In the first exothermic phase of the reaction, cold water cooling was used. By the end of the 3-hr. reaction period, a crystalline precipitate had formed. This was removed by filtration and recrystallized from toluene to yield 9.7 g. (35.8%) of *exo*-2-*p*-chlorophenylsulfinyl - 3 - hydroxy - *endo* - 5,6,7,8,9,9 - hexachloro - *exo*-*endo* - 1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8 - dimethanonaphthalene of m.p. 248–249° dec. (XIX). Another crystalline hydroxy sulfoxide isomer was obtained from the toluene filtrate by concentration and recrystallization. This isomer (5.5 g., 20.3%) had an m.p. of 207–210° (XX). Also obtained from the mother liquor was 0.5 g. (4%) of the sulfide addition product, *exo* - 2 - *p* - chlorophenylmercapto - *endo*-5,6,7,8,9,9 - hexachloro - *exo* - *endo* - 1,2,3,4,4a,5,8,8a,-octahydro-1,4,5,8-dimethanonaphthalene (IX). Some analytical data and physical properties of the sulfoxide isomers are shown in Tables IV and V.

Separation of the intermediate hydroperoxide. Into 162 ml. of *n*-pentane solution of 3.62 g. (0.025 mole) of 4-chlorobenzenethiol and 9.12 g. (0.025 mole) of Aldrin, air was introduced while it was irradiated from 5-cm. distance with an ultraviolet lamp and cooled by an ice-water bath. After 5 min., the precipitation of a white fluffy crystalline product started. The ultraviolet initiation was removed after 5 more min. After a total of 30 min. of air introduction, the crystals were removed by filtration, washed with *n*-pentane and dried in a vacuum desiccator. In this manner, 2 g. (15.4%) of *exo* - 2 - *p* - chlorophenylmercapto - 3 - hydroperoxy - *endo*-5,6,7,8,9,9-hexachloro-*exo*-*endo*-1,2,3,4,4a,5,8,8a - octahydro-1,4,5,8-dimethanonaphthalene (XVIII) was obtained. The peroxide content of this hydroperoxide was found to be 91% as determined by the iodide method. On heating, it melted at 116–119°. Then it solidified again and melted again with decomposition between 240–242°. Some physical and analytical properties of the compound are given in Tables IV and V.

Further introduction of air into the filtered reaction mixture resulted in the precipitation of a hydroperoxide (XVIII)–hydroxy sulfoxide (XIX, XX) mixture.

Rearrangement of the hydroperoxide. A carbon tetrachloride solution (15 ml.) of 0.27 g. of *exo*-2-*p*-chlorophenylmercapto-3 - hydroperoxy - *endo* - 5,6,7,8,9,9 - hexachloro - *exo* - *endo*-1,2,3,4,4a,5,8,8a- octahydro - 1,4,5,8 - dimethanonaphthalene (XVIII) was left to stand at room temperature. By the end of this time, the strong peroxide reaction of the original solution disappeared and fine needles of a white crystalline solid precipitated. These crystals (0.18 g.) after filtration and drying had a m.p. of 246–248° and showed no depression on the determination of mixed melting point with *exo*-2-*p*-chlorophenylsulfinyl - 3 - hydroxy - *endo* - 5,6,7,8,9,9-hexachloro - *exo* - *endo* - 1,2,3,4,4a,5,8,8a - octahydro-1,4,5,8-dimethanonaphthalene (XIX).

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