[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Oxidation of Unsaturated Compounds. III. Products of the Reaction of Indene and Oxygen; Stereochemistry of the Addition of a Peroxy Radical and Oxygen to a Double Bond[1]

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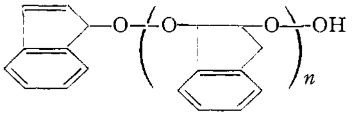
Indene and oxygen react in the presence or absence of free radical initiators to produce a polymeric peroxide containing alternating indene and oxygen units. Reduction of indene peroxide with lithium aluminum hydride yields *cis*- and *trans*-indene glycols in nearly equal amounts, indicating that the addition of a peroxy radical and an oxygen molecule to the double bond of indene has a very low stereospecificity. About 40 chain transfer reactions occur for each chain termination in the oxidation of indene. The mechanism of the chain transfer reaction and the nature of the chain endings thus formed is discussed. Indene peroxide is rearranged to 3-isochromanone by treatment with strong bases followed by acidification. This behavior is taken as further evidence of the copolymer structure of indene peroxide and a reaction sequence that accounts for the formation of 3-isochromanone is proposed.

Others papers in this series have demonstrated that the low temperature, liquid phase oxidation of an olefin containing an activated double bond (*e.g.*, styrene) involves a free radical copolymerization of oxygen and the olefin.[2] For example, the reaction of styrene and oxygen at 50° produces a polymer that decomposes explosively. Reduction of this polymer by lithium aluminum hydride produces phenylethylene glycol in high yields thereby confirming the structure of styrene peroxide as a 1:1 copolymer.[3] Non-polymerizable olefins or aromatic hydrocarbons with activated hydrogen atoms, such as cyclohexene and tetralin, react with oxygen to form hydroperoxides. Here the slow propagation step involves the abstraction of a hydrogen atom by a peroxy radical.[4]

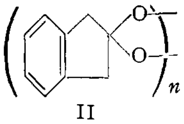
In the case of indene, both of these reactions are possible and the formation of both hydroperoxide and polymeric peroxides would be expected. Thus, the reaction of indene and oxygen should produce the products generalized by I.



I

The reaction of indene with molecular oxygen has been investigated previously by Gutmann,[5] and by Hock,[6] but many of their conclusions are not consistent with the interpretation given above. Gutmann's conclusions that polyindene and polymeric indene peroxide are formed concurrently in the oxidation of indene, and that oxygen accelerates the polymerization of indene to produce polyindene containing only two atoms of oxygen per molecule,[5] are difficult to comprehend if both the polymerization and oxidation proceed by a free radical mechanism. Since Gutmann reported separating polyindene from polymeric indene peroxide by precipitation of polyindene by methyl alcohol, whereas it has been reported that the alcohol-insoluble fraction obtained in the oxidation of indene is very rich in oxygen,[7] it was thus considered worthwhile to repeat this work.

Moreover, the proposals by Hock as to the mechanism of the thermal or photoöxidation of indene and the structure of the polymeric peroxide formed,[6] do not support Gutmann's conclusion that the polymeric peroxide formed in the oxidation of indene is the copolymer of indene and oxygen. However, the evidence of Hock that the polymeric peroxides formed in the oxidation of indene are cyclic trimeric and hexameric 2-indanone peroxides (II, $n = 3, 6$) is weak since the only evidence presented was empirical analysis, molecular weight and reduction with zinc and hydrochloric acid to 2-indanone in 15% yield.



II

Results and Discussion

In the first section the separation and analysis of the products of the oxidation of indene will be discussed. It will be shown that the products obtained are in general agreement with I and that polyindene is not formed concurrently with indene peroxide. Next the mechanism of chain transfer will be considered and evidence presented for a transfer reaction other than the abstraction of an α-hydrogen atom. The third section will discuss the reduction of indene peroxide. The data presented here confirm I and exclude II as the structure of indene peroxide. The reduction products of indene peroxide also demonstrate that the addition of a peroxy radical and an oxygen molecule to indene has a very low stereospecificity and the stereochemistry of free radical additions to double bonds in general is discussed. Finally, in the last section, the decomposition of indene peroxide by base to yield 3-isochromanone upon acidification will be discussed.

Products of the Oxidation.—The reaction of indene with oxygen at 50° in the presence of free

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(1) Previous paper in this series. F. R. Mayo and A. A. Miller, THIS JOURNAL, **78**, 1023 (1956).

(2) (a) A. A. Miller and F. R. Mayo, *ibid*., **78**, 1017 (1956); (b) A. A. Miller, F. R. Mayo and G. A. Russell, unpublished results; see also C. E. Barnes, R. M. Elofson and G. D. Jones, *ibid*., **72**, 210 (1950).

(3) G. A. Russell, *ibid*., **75**, 5011 (1953).

(4) J. L. Bolland, *Quart. Revs.* (*London*), **3**, 1 (1949); L. Bateman, *ibid*., **8**, 147 (1954); G. A. Russell, THIS JOURNAL, **77**, 4583 (1955); **78**, 1041 (1956).

(5) V. Gutmann, *J. Polymer Sci*., **3**, 336, 518, 646 (1948).

(6) H. Hock and S. Lang, *Ber*., **77B**, 257 (1944); H. Hock, S. Lang and G. Knauel, *ibid*., **83**, 227 (1950); H. Hock and F. Depke, *ibid*., **84**, 122 (1951).

(7) M. Weger and A. Billmann, *ibid*., **36**, 640 (1903).

TABLE I

PRODUCTS OF OXIDATION OF INDENE AT 50°

Fraction	Wt., g.	% O_2[a]	$C_9H_8:O_2$[b]	Mole of reactants		Mol. wt.[c]	% of oxygen as peroxide[d]	End groups/molecule	
				Oxygen	Indene			—OOH[e]	>C=C<[f]
A	2.29	21.0	1.03:1	0.015	0.015	..	100	..	..
B	0.38	20.5	1.05:1	.002	.002	..	(~100)	..	..
C	1.94	18.9	1.15:1	.011	.013	1760	(~ 86)	..	..
D	4.37	18.3	1.18:1	.025	.030	1700	85.6	0.53	0.88
E	10.81	21.1	1.03:1	.071	.073	627	79.0	.28	.90
F	3.36	20.8	1.04:1	.022	.023	328	73.0	.12	.58
G	0.57	20.2	1.07:1	.004	.004	..	..	..	..
Recovd. indene	41.7				.359				

[a] Calculated from % C and % H. [b] Mole ratio calculated from % C. [c] Determined crysocopically in benzene solution. [d] From reaction with hydriodic acid at 80–100°. [e] From reaction with hydriodic acid in isopropyl alcohol at 25°. [f] From reaction with bromine in carbon tetrachloride solution; corrected for substitution.

radical initiators, or at 60° in the absence of catalysts, produces peroxides with a variety of physical properties. When 0.53 mole of indene containing 0.02 *M* α,α'-azodiisobutyronitrile was vigorously agitated at 50° with 730 mm. of oxygen, 0.153 mole of oxygen was absorbed in 12 hours. The products were fractionated into the seven fractions listed in Table I. These fractions represent material insoluble in benzene (A), sparingly soluble in benzene (B), easily precipitated from benzene by methyl alcohol (C, D), easily precipitated from benzene by petroleum ether but not by methyl alcohol (E), insoluble in petroleum ether at −20° (F), and slightly soluble in petroleum ether at −20° (G). Fraction A was a white solid melting at 125–130° while fractions B-E were solids with indefinite melting points. Fractions F and G were viscid oils at room temperature which would not crystallize upon cooling. All of these fractions liberated iodine from constant boiling hydriodic acid at 80–100° and burned with considerable violence and sputtering.

The fractions listed in Table I account for 98% of the oxygen absorbed and indene used. Similar products were obtained in uncatalyzed oxidations at 60°. Moreover, kinetic evidence suggests that both the catalyzed and uncatalyzed reactions proceed by the same active intermediates and therefore should yield the same products.[8]

The methanol-insoluble material formed in the oxidation of indene (A) is evidently not polyindene since only a little more than one molecule of indene is present per molecule of oxygen. In general, the data summarized in Table I agree with those of Hock.[6] However, whereas Hock claimed the benzene-soluble polymers to be trimeric and hexameric 2-indanone peroxides (mol. wt. 444 and 888), the molecular weights of the fractions obtained in the present work varied considerably with the isolation techniques used and there was no evidence that pure compounds could be isolated easily.

The lowest molecular weight material (G) was examined for the presence of a monomeric peroxide or hydroperoxide. The infrared spectrum of this fraction indicated the presence of hydroxyl, carbonyl and olefinic groups in addition to the peroxide bond and the aromatic ring. Attempts to crystallize this material from various solvents were unsuccessful. A slow distillation at 10^{-5} mm. yielded no volatile peroxidic products but resulted in decomposition with the formation of water. This result indicates the presence of hydroperoxide groups in this material, possibly as indenyl hydroperoxide.

No satisfactory method is known by which the peroxide content of a very stable polymeric peroxide, like indene peroxide, can be determined. The best method found was a modification of the method previously used for determining di-*t*-butyl peroxide,[9] and involved the addition of either the solid indene peroxide or its solution in acetic anhydride to constant boiling hydriodic acid at 80–100° in a carbon dioxide atmosphere. This method gave a very rapid liberation of iodine over a period of about two minutes followed by a slower, nearly linear liberation of iodine. The slow liberation of iodine presumably involved the reaction of hydriodic acid with the products of the first rapid reaction. Analyses were thus performed by plotting the amount of iodine liberated as a function of time and extrapolating the linear portion of the curve to zero time. By this method the data of column 8 of Table I were obtained.

In an attempt to obtain information on the nature of the chain endings, fractions D-F were analyzed for active oxygen by the method of Kokatnur and Jelling,[10] an excellent procedure for the analysis of hydroperoxides and acyl peroxides but inadequate for most dialkyl peroxides. When subjected to this analysis indene peroxide rapidly liberated iodine equivalent to only a small portion of the total peroxidic oxygen. Furthermore, after the rapid liberation of a small amount of iodine the rate of iodine formation became insignificant. The iodine thus liberated has been entered in column 9 of Table I as a measure of the hydroperoxide content of the polymer. These data indicate that indene peroxide contains considerably less than one hydroperoxide end group per molecule. Infrared spectra substantiated this interpretation since hydroxyl and carbonyl groups as well as ethylenic unsaturation were found in fractions A-G. Moreover, the absorption due to these groups became more pronounced as the molecular weight of the polymer decreased.

An attempt also was made to determine the

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(8) G. A. Russell, THIS JOURNAL, **78**, 1041 (1956).

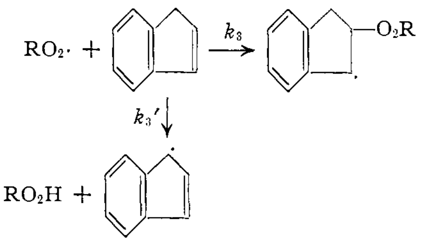
(9) F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Treseder and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

(10) V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

unsaturation of the polymeric peroxides. Fractions D-F reacted readily with bromine in carbon tetrachloride solution but more substitution than addition occurred. A correction for the bromine reacting by substitution was made by the use of potassium iodate.[11] The data thus obtained are entered in the right-hand column of Table I and show that in fractions D and E very nearly one double bond is present per molecule.

The benzene-insoluble fractions (A and B) formed in the oxidation of indene merit some special attention. Fraction A had a solubility in benzene at 25° of only 1.2 g./liter and melted over a rather narrow range (125–130°) without apparent decomposition. However, decomposition became evident a few degrees above the melting point. These fractions had the appearance of a crystalline material under crossed polaroids, whereas fractions C and D did not. As the analysis of fractions A and B approaches that of a 1:1 copolymer of oxygen and indene more closely than the high molecular weight benzene-soluble fractions (C and D), the insolubility observed for fractions A and B may not necessarily signify a very high molecular weight, nor a structure particularly different from the soluble fractions, but may result because a 1:1 oxygen ratio favors a crystalline structure. The very low solubility of fraction A in some fifteen solvents tested including N,N-dimethylformamide, acetic anhydride, naphthalene (80°), acetamide, ethylene dibromide, ketones, ethers and aromatics is in itself an indication of crystallinity. Moreover, as would be expected for a crystalline material, a chlorobenzene or a cumene solution of A, saturated at 80°, precipitated material when cooled to room temperature.

The analysis, molecular weight and properties of the materials formed in the oxidation of indene at 50° indicate that in general the products of the oxidation are described by I. The degree of polymerization observed, $n + 1$, averages less than 10. This indicates that a chain transfer reaction competes significantly with the polymer-forming reaction. From the distribution of molecular weights reported in Table I, an approximate ratio of k_3 to k_3' of about 4 to 1 is indicated if all of the chain transfer is assumed to occur by hydrogen atom abstraction. This ratio of rate constants predicts that about 5% of the oxygen absorbed should be found as monomeric indenyl hydroperoxide.



Nature of the Chain Transfer Reaction.—The structure of the polymeric fractions may be somewhat more complex than I. Although olefinic unsaturation equivalent to that expected from I was found, the hydroperoxide content of the polymers was considerably below the expected value. Furthermore, the percentage of oxygen present a speroxidic oxygen decreased with molecular weight, suggesting that at least a portion of the end groups present contained oxygen in some form other than hydroperoxide. Infrared absorption indicated the presence of carbonyl groups and possibly also hydroxyl groups in addition to hydroperoxide groups, and it seems likely that these functions are chain endings in some of the molecules. These chain endings could conceivably be formed by either the decomposition of hydroperoxide end groups, a chain transfer reaction different from 3', a chain termination reaction or a degradation of high molecular weight indene peroxide molecules.

Several of these possibilities can be excluded as important reactions. The chain termination reaction cannot play an important role in the formation of end groups since the kinetic chain length is much greater than the degree of polymerization. Thus, in the presence of 0.01 M α,α'-azodiisobutyronitrile at 50° and 730 mm. oxygen pressure, the rate of oxygen absorption by indene is 0.081 mole $l.^{-1}$ $hr.^{-1}$.[8] At this temperature the rate of production of free radicals from 0.01 M α,α'-azodiisobutyronitrile in benzene solution is 0.000190 mole $hr.^{-1}$,[12] and the ratio of these values, 430, is the kinetic chain length or the number of oxygen molecules reacting per initiator radical formed. This value for the kinetic chain length is probably somewhat high because of a thermal initiation reaction in the oxidation of indene.[8] Comparable values of kinetic chain lengths for the copolymerization of oxygen with styrene, α-methylstyrene, 1,1-diphenylethylene and methyl methacrylate at 50° in the presence of 0.01 M α,α'-azodiisobutyronitrile are 320, 630, 95 and 33, respectively.[2b] Thus the oxidation of indene gives a quite respectable chain length and more than 40 chain transfer reactions occur for each chain termination reaction. Therefore, end groups resulting from chain termination cannot account for more than about 2% of the total end groups present.

The possibility of chain degradation of high molecular weight peroxide molecules also may be excluded as a major reaction in the production of end groups since it has been observed that the average degree of polymerization in the oxidation of indene does not decrease significantly with an increase in the degree of oxidation.[5] The decomposition of hydroperoxides to give carbonyl or hydroxyl end groups should result in the formation of water, a product not observed in the oxidation of indene. Moreover, the temperatures employed (50°) are considerably below those needed to decompose similar hydroperoxides, such as cyclohexenyl or tetralyl hydroperoxides, at a significant rate.

Thus, it appears most likely that end groups other than hydroperoxide and indenyl are formed in a chain transfer reaction. Because of the lack of sufficient data the nature of this chain transfer

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[11] H. P. Groll, G. Hearne, F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939).

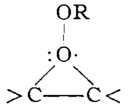
[12] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951); see also G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

reaction is not understood. Presumably it is similar to the unknown chain transfer reaction observed in the copolymerization of styrene or α-methylstyrene with oxygen.[2]

Stereochemistry.—The reduction of indene peroxide was investigated as a proof of structure and also to determine the stereochemistry of the addition of a peroxy radical and an oxygen molecule to a double bond. The reduction of polymeric indene peroxide of molecular weight 1500 by lithium aluminum hydride produces very nearly one equivalent of hydrogen and destroys one-half equivalent of lithium aluminum hydride per peroxide link, a behavior similar to that observed for styrene and α-methylstyrene peroxides.[3] The products of this reaction are mainly *cis*- and *trans*-indene glycols supporting I and not II as the structure of indene peroxide. Hock considered the polymeric peroxides formed in the oxidation of indene to be polymeric 2-indanone peroxides mainly on the evidence that 2-indanone could be obtained by treatment of the polymers with zinc and hydrochloric acid.[6] Reduction by zinc and hydrochloric acid is misleading because the primary reduction products, indene glycols, are converted to 2-indanone by treatment with dilute acids.[13]

To determine the ratio of *cis*- and *trans*-indene glycol formed in the reduction, and thus the stereochemistry of the addition of a peroxy radical and oxygen to a double bond, an oxidation of indene similar to that summarized in Table I was performed and all of the products insoluble in petroleum ether were reduced. This sample of indene peroxide, having an indene–oxygen ratio of 1.05:1, dissolved rapidly with the evolution of hydrogen when added to an ether solution of lithium aluminum hydride. When the reaction had ceased the reaction mixture was hydrolyzed but never acidified. The yield of purified glycols isolated from the reaction product was 62% while 70% of the theoretical hydrogen was evolved. The glycols formed were easily separated by solubility differences to give nearly equal amounts of *cis*- and *trans*-indene glycol.

The formation of equivalent amounts of *cis*- and *trans*-glycols indicates that the addition of a peroxy radical and an oxygen molecule to the double bond of indene has a very low stereospecificity. Moreover, intermediates of the type



cannot possess sufficient stability to play an important role in the oxidation of indene since this intermediate would predict the formation of only the *trans*-peroxide. It has been proposed that similar bridged structures are important in the free radical addition of hydrogen bromide to olefins.[14] However it would seem that if a bromine atom can bridge two carbon atoms an oxygen atom of a peroxide group should form a similar intermediate.

The free radical additions of hydrogen bromide,[14] hydrogen sulfide,[15a] thiophenol[15a] and thioacetic acid[15] to 1-substituted cyclohexenes are known to occur with nearly complete *trans*-stereochemistry to produce what is often the less stable product. Furthermore, radical copolymerizations of *cis*- and *trans*-2-butene with sulfur dioxide,[16a] and possibly maleate and fumarate esters with vinyl acetate[16b] yield polymers having different heat contents. On the other hand, the additions of bromotrichloromethane to *cis*- and *trans*-2-butene[17] or the copolymerization of vinyl acetate with *cis*- and *trans*-dichloroethylene[16c] produce the same mixtures of products. Thus, it appears that the addition of free radicals to a double bond does not always follow one stereospecific mode of addition.

The addition of a peroxy radical and an oxygen molecule to the double bond of indene should produce a more stable product if the two peroxy groups occupied *trans* positions. However, the formation of nearly equal amounts of *cis* and *trans* adducts is readily explained. Although it is not certain that all free radicals are planar,[18] the 2-peroxy-1-indanyl radical formed by the addition of a peroxy radical to the double bond of indene almots certainly must be planar. Since the subsequent reaction of a free alkyl radical with oxygen is a fast exothermic reaction, requiring no activation energy in the case of a 1-tetralyl radical,[19] the transition state should closely approximate the reactants,[20] and the stabilities of the products will not affect the orientation of the reactants in the transition state. Thus the carbon–oxygen bond is only partially formed in the transition state for the reaction of an oxygen molecule with a 2-peroxy-1-indanyl radical and there is evidently no steric effect favoring a *trans* orientation of the two peroxy groups. On the other hand, the addition of a trichloromethyl radical to the double bond of an olefin produces a radical that does not necessarily react in an exothermic manner with bromotrichloromethane. Here the stabilities of the products of the reaction undoubtedly contribute to the energies of the transition states and the addition of bromotrichloromethane[21] or ethyl bromoacetate[21b] to cycloalkenes or other olefins[17] thus yields the more stable adduct as the major product. The mechanisms of stereospecific additions that produce major amounts of the less stable adducts appear unsettled. Some of the second steps in these additions are highly exothermic (*e.g.*, alkyl radicals reacting with mercaptans) and may involve transition states

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[13] Fr. Heusler and H. Schieffer, *Ber.*, **32**, 28 (1899); H. D. Porter and C. M. Suter, THIS JOURNAL, **57**, 2022 (1935).

[14] H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952); H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

[15] (a) H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956); (b) F. G. Bordwell and W. A. Hewett, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York City, September, 1954, p. 6-O.

[16] (a) G. M. Bristow and F. S. Dainton, *Proc. Roy. Soc.*, **229A**, 509, 525 (1955); (b) L. K. J. Tong and W. O. Kenyon, THIS JOURNAL, **71**, 1925 (1949); (c) F. R. Mayo and K. E. Wilzbach, *ibid.*, **71**, 1124 (1949).

[17] P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

[18] G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

[19] C. H. Bamford and M. J. S. Dewar, *Proc. Royal Soc.* (*London*), **198A**, 252 (1949).

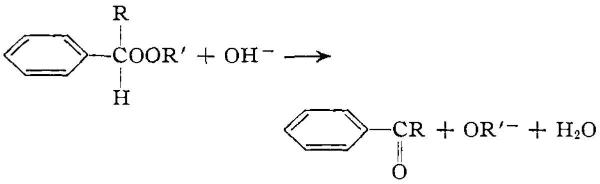
[20] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[21] (a) E. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950); M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949); (b) J. Weinstock, Abstracts of Papers, 128th Meeting of the American Chemical Society, Minneapolis, Minn., Sept 1955, p. 19-O.

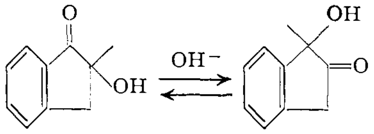
that resemble the reactants and are similar to the one proposed for the reaction of oxygen with an indanyl radical. In these cases high yields of the less stable isomer may result because of preferred configurations of the radicals and steric effects involved in approach to the radical.[14,15a] In some other cases complexes between the olefin and the addend may play important roles in determining the stereochemistry of the adduct.[14] This suggestion is particularly pertinent to the copolymerization of olefins with sulfur dioxide since in these systems 1:1 complexes are known to exist.[16a]

Decomposition of Indene Peroxide by Base.—Hock reported that treatment of polymeric indene peroxide with strong bases, followed by acidification produced 3-isochromanone (III).[6] This behavior has been verified. Moreover, it has been observed that the yield of III increases and the yield of resinous material formed decreases with the molecular weight of the polymer. Thus, fraction A produced 61% of purified III while fraction E yielded less than 30% under similar conditions. This behavior supports the conclusion that the end groups of the polymer give rise to the resinous material and that III is formed by the attack of base on the repeating units of the chain.

The formation of III from indene peroxide is additional evidence that I and not II represents the structure of indene peroxide. Although it would be difficult to formulate a reaction producing III from II, it is not a surprising product from the reaction of I with base. Kornblum and DeLaMare have shown that bases readily catalyze the decomposition of alkyl peroxides to ketones and alcohols when the peroxide contains hydrogen atoms alpha to both the phenyl and the peroxide group.[22]

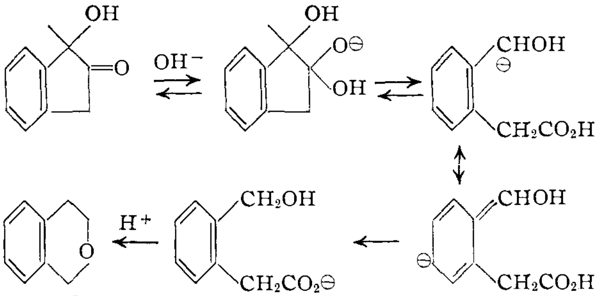


In the case of I the major product expected from base-catalyzed decomposition would be the α-ketol (IV) which in basic solution isomerizes readily to V.[23]



IV V

Since α-ketols are known to be readily, and sometimes quantitatively, cleaved by bases to acids and alcohols,[24] the formation of III from I may occur as



III

It is perhaps surprising that the decomposition products isolated appear to come from V and not from IV since the equilibrium between IV and V should favor IV because of the possibility of conjugation of the carbonyl group with the aromatic ring. However, the carbanion intermediate from V, but not from IV, can be stabilized by resonance with the aromatic ring.

Experimental

Indene.—Schering–Kahlbaum indene was distilled at 100 mm. through a Podbielniak column (<50 plates). A fraction boiling constantly at about 114° (boiling point measured by an uncalibrated thermocouple) and having $n^{20}D$ 1.5764 was used; lit.[25] b.p. 114.5° (100 mm.), $n^{20}D$ 1.5763. The freezing point of this material was determined by a 9-junction calibrated copper–constantan thermocouple and a Rubicon portable potentiometer to be −0.96 to −1.10°. This freezing point is somewhat higher than the freezing point reported for indene isolated from commercial grade indene, −1.80°,[25] and −1.2 to −1.6°.[8]

Oxidation Procedure.—Indene was oxidized in a closed system in a modified 250-ml. erlenmeyer flask that was shaken vigorously in a water-bath. The oxygen absorption was followed by use of a wet-test meter and a correction applied for water vapor. Oxygen from the wet-test meter was dried by passage through a Dry Ice trap. At the end of the oxidation summarized in Table I, a sample of the vapor in contact with the indene was analyzed by a mass spectrometer. Only indene and oxygen were found in appreciable quantities. Similar oxidations at 60° produced small amounts of carbon dioxide. The amount of agitation provided was sufficient so that an increase or decrease in the rate of shaking did not affect the rate of oxidation.

Fractionation of Indene Peroxide.—Fractions A–G listed in Table I were isolated in the following manner. The oxidation product, which contained a white precipitate, was washed from the oxidation flask with 25 ml. of benzene and added to 90 ml. of absolute methyl alcohol. The solid formed was extracted with four 50-ml. portions of benzene to give a residue (A) sparingly soluble in benzene. The benzene washings were evaporated to 20 ml., filtered and the solid collected washed with two 25-ml. portions of benzene to give the solid residue B. The benzene filtrate and washings were combined and evaporated to 20 ml. and C precipitated by the addition of 60 ml. of methyl alcohol. The filtrate, obtained from the first methyl alcohol precipitation of crude indene peroxide, was evaporated at room temperature (0.5 mm.) for 16 hours and the residue (*ca.* 40 ml.) added to 100 ml. of petroleum ether. The precipitate was twice precipitated from 20 ml. of benzene by 50 ml. of methyl alcohol to give fraction D. The filtrates from fractions C and D were combined and the solvents removed by evacuation at 0.5 mm. The residue precipitated an oil when added to 75 ml. of petroleum ether and this oil was reprecipitated from 20 ml. of benzene as solid E by 75 ml. of petroleum ether. All of the filtrates were again combined, the solvents removed at 0.5 mm. and the oil that remained added to 100 ml. of petroleum ether at −30°. An oil was precipitated which was removed, treated with 100 ml. of petroleum ether at 25° and then cooled to −20° to give the insoluble oil F. All of the filtrates were again combined and evacuated to give fraction G. All fractions were evacu-

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[22] N. Kornblum and H. E. DeLaMare, THIS JOURNAL, **73**, 880 (1951).

[23] C. Schöpf and R. Kühne, *Ber.*, **83**, 390 (1950); see also K. Auwers, H. Ludewig and A. Müller, *Ann.*, **526**, 143 (1936).

[24] F. S. Acree, *Am. Chem. J.*, **29**, 588 (1904), *Ber.*, **37**, 2753 (1904); D. Y. Curtin and J. Leskowitz, THIS JOURNAL, **73**, 2633 (1951); D. B. Sharp and E. L. Miller, *ibid.*, **74**, 5643 (1952); see also R. G. Pearson and R. L. Dillon, *ibid.*, **70**, 1933 (1948); R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926, 931 (1951); R. G. Pearson, D. H. Anderson and L. L. Alt, *ibid.*, **77**, 527 (1955).

[25] E. S. Naidus and M. B. Mueller, *ibid.*, **72**, 1829 (1950).

ated to constant weight in the dark at room temperature and 10^{-5} mm. before being weighed or analyzed. The solvents and unreacted indene that had been distilled during the various vacuum treatments were collected in Dry Ice traps and distilled to obtain unreacted indene.

Analytical Procedures.—Peroxidic oxygen was determined by adding fractions A or B or an aliquot of an acetic anhydride solution of fractions C-G to 2 ml. of constant boiling hydriodic acid at 80° under a carbon dioxide atmosphere. After an appropriate interval, the reaction mixtures were diluted to 50 ml. with water and titrated with 0.1 *N* thiosulfate solution. If sufficient reaction time was allowed, the amount of iodine liberated could exceed more than 1 mole per mole of oxygen present. The amount of iodine equivalent to the peroxide oxygen was thus taken as the extrapolated value at zero time. In Table II, the analytical data, obtained for fraction F in this manner and by the method of Kokatnur and Jelling,[10] are summarized. Blank corrections were applied.

TABLE II

PEROXIDE ANALYSIS OF INDENE PEROXIDE (FRACTION F)

Time, min.	Peroxidic oxygen, % of theory[a]	Hydroperoxides,[b] wt. %
0	70.2[c]	
1	70.7	
2	72.2	3.15
4	74.2	
5		4.84
6	76.1	
10		5.54
15		5.54

[a] 1 ml. of a 5% acetic anhydride solution per 2 ml. of hydriodic acid. [b] 1 ml. of a 5% benzene solution, 1 ml. of a saturated potassium iodide solution and 1 ml. of glacial acetic acid in 50 ml. of 99% isopropyl alcohol. [c] Extrapolated value.

Unsaturation was determined by reaction with a standard solution of bromine in carbon tetrachloride by a procedure identical to that described by Mayo.[11,26]

Preparation of 3-Isochromanone from Indene Peroxide.—Fraction A (0.90 g.) was stirred with 20 ml. of aqueous 20% potassium hydroxide at 25° for 18 hours to give a clear solution and 0.08 g. of tar. Acidification of the clear solution with concd. hydrochloric acid produced 0.10 g. of tar and caused the solution to become cloudy. After 18 hours at 0°, 0.60 g. of material had crystallized. Recrystallization from benzene and petroleum ether gave 0.55 g. of 3-isochromanone melting at 81–83° (reported[6] m.p. 83°) and having a saponification equivalent of 147 (theory (148)).

Anal. Calcd. for $C_9H_8O_2$: C, 73.0; H, 5.4. Found: C, 73.0; H, 5.6.

Reduction of Indene Peroxide.—A slurry of 10 g. of indene peroxide, containing 95.0% of the theoretical oxygen, in a mixture of 100 ml. of ethyl ether and 50 ml. of benzene was added with stirring to 5 g. of lithium aluminum hydride in 50 ml. of ether under a nitrogen atmosphere at 0°. The undissolved indene peroxide rapidly dissolved with the evolution of hydrogen which was measured by a wet test meter separated from the reaction flask by a Dry Ice trap. A total of 0.45 mole of hydrogen was liberated after one hour at 0° followed by an hour of reflux. The evolution of hydrogen essentially ceased after all of the peroxide had been added.

The reduction products were hydrolyzed rapidly, first with methyl alcohol and then with a saturated ammonium chloride solution. The ether, methyl alcohol and water were removed under reduced pressure to give a solid residue that was extracted for 24 hours in a Soxhlet extractor by 500 ml. of ether. During the extraction a solid crystallized from the ether. The ether solution was evaporated to 50 ml. and filtered to give 3.2 g. of *trans*-indene glycol, m.p. 157–158° (cor.) (reported[27] m.p. 159.8–160°).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.9; H, 6.7. Found: C, 72.1; H, 6.6.

Removal of the ether from the filtrate left 5.65 g. of an oil of which 3.77 g. readily dissolved in hot water. The water was removed to give an oil that still could not be crystallized. Distillation at 0.6 mm. yielded 2.9 g. of material boiling at 133–137° which crystallized upon standing. This material was readily soluble in ethyl ether and could be crystallized from it. The *cis*-indene glycol obtained melted at 105–106° (cor.) (reported[27] m.p. 107.5–108°).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.9; H, 6.7. Found: C, 72.0; H, 6.5.

A sample of *cis*-indene glycol was converted to 2-indanone by treatment with dilute acid.[13] A sample weighing 0.152 g. was warmed to 60° with 50 ml. of 2 *N* sulfuric acid for 14 hours. An aliquot of the solution was treated with an excess of 2,4-dinitrophenylhydrazine reagent, heated on a hot-plate for five minutes, filtered and dried to give a hydrazone equivalent to 0.31 g. from the starting glycol. This represented 98% of the theoretical hydrazone of 2-indanone. The hydrazone decomposed on heating.[13] Further heating of the acidic solution of *cis*-indene glycol for eight hours did not increase the amount of hydrazone formed.

SCHENECTADY, N. Y.

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[26] F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953).

[27] J. Böeseken and C. van Loon, *Proc. Acad. Sci., Amsterdam*, **20**, 1186 (1918).