THE CHEMISTRY OF HYDROPEROXIDES. VIII. THE ACID-CATALYZED DECOMPOSITION OF CERTAIN HYDROPEROXIDES

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Objectives of the research. The work hereinafter described was undertaken for the purpose of clarifying and extending the general theory of acid-catalyzed hydroperoxide decomposition (1), with special attention to: (a) the nature of the decomposition of hydroperoxides other than the tertiary, (b) the relation of hydroperoxide structure to stability with respect to acid-catalyzed decomposition, and (c), the relative migratory aptitudes of groups participating in incidental rearrangements.

1-Tetralyl, 3-cyclohexenyl, and α-p-xylyl hydroperoxides were selected for study as representative secondary and primary hydroperoxides because of their ready availability. In each case, when reaction was conducted in glacial acetic acid and catalyzed by perchloric acid, the products predictable upon the basis of the reaction mechanism previously proposed were isolated, notwithstanding reports of the formation of other products of supposedly acid-catalyzed reactions carried out under other conditions.

In pursuit of the second and third objectives stated use was made of the experimentally convenient method of treating a tertiary alcohol with hydrogen peroxide in the presence of a strong acid, which served to catalyze both peroxide formation and peroxide decomposition. As concerns the question of group migratory aptitudes the method has as yet been applied only in a preliminary exploratory manner (1).

Incidentally, it has been shown that by the substitution of organic hydroperoxides for hydrogen peroxide the method may be extended to a study of the acid-catalyzed decomposition of unsymmetrical peroxides.

The acid-catalyzed decomposition of 1-tetralyl hydroperoxide. It has been previously reported that the addition of a single drop of concentrated sulfuric acid initiates explosive decomposition of 1-tetralyl hydroperoxide (2). More carefully controlled acid decomposition in alcoholic solution at 80° led to a dark-brown resinous product substantially insoluble in aqueous sodium carbonate but soluble in aqueous sodium hydroxide. A small amount of γ-(o-hydroxyphenyl)butyric acid was recovered from the sodium carbonate extract (3).

In the present study the catalyzed decomposition of 1-tetralyl hydroperoxide was effected in glacial acetic acid solution with the aid of perchloric acid (0.1 mole-%). The major product was a brown resinous material similar to that described by Hock and Lang (3), which was identified as consisting essentially of the aldol of γ-(o-hydroxyphenyl)butyraldehyde. The alkali-insoluble products formed in small quantities appeared to be acetates of 1-tetralone.
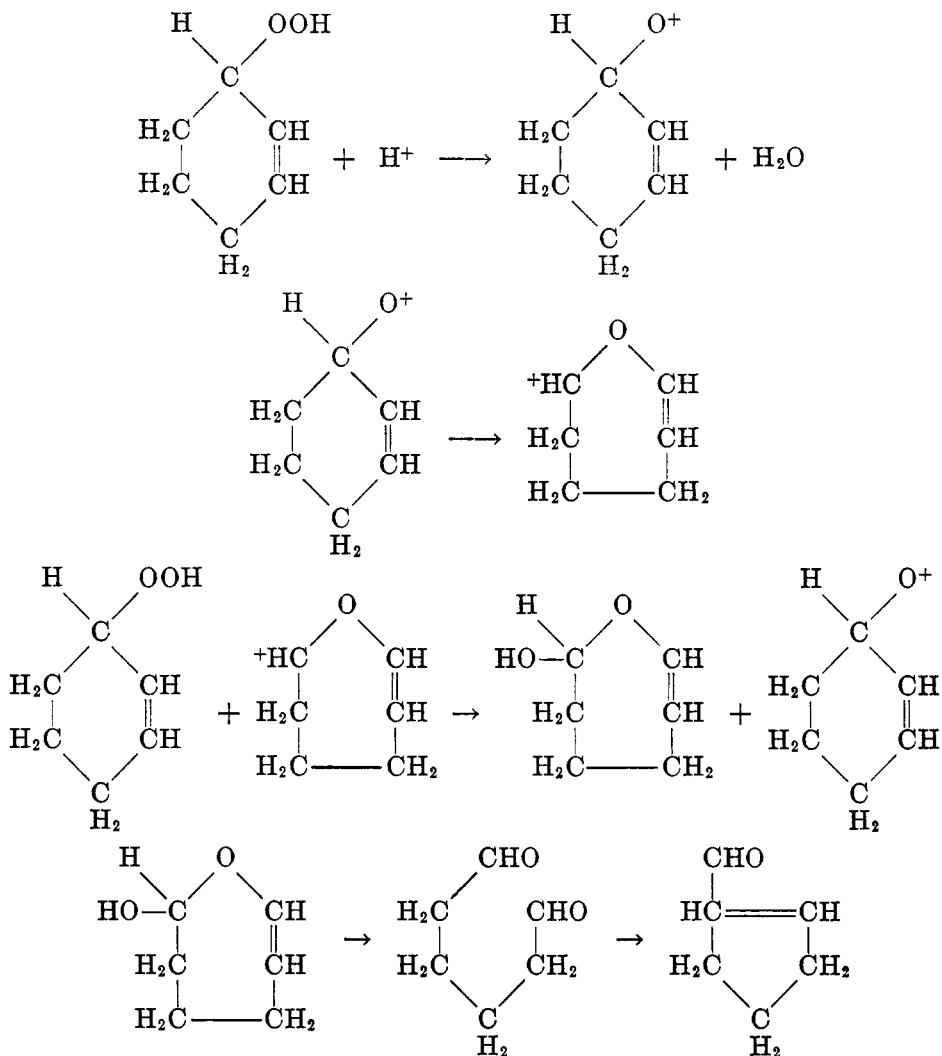
On the basis of the reaction mechanism previously proposed, the expected primary decomposition product would be γ-(o-hydroxyphenyl)butyraldehyde.
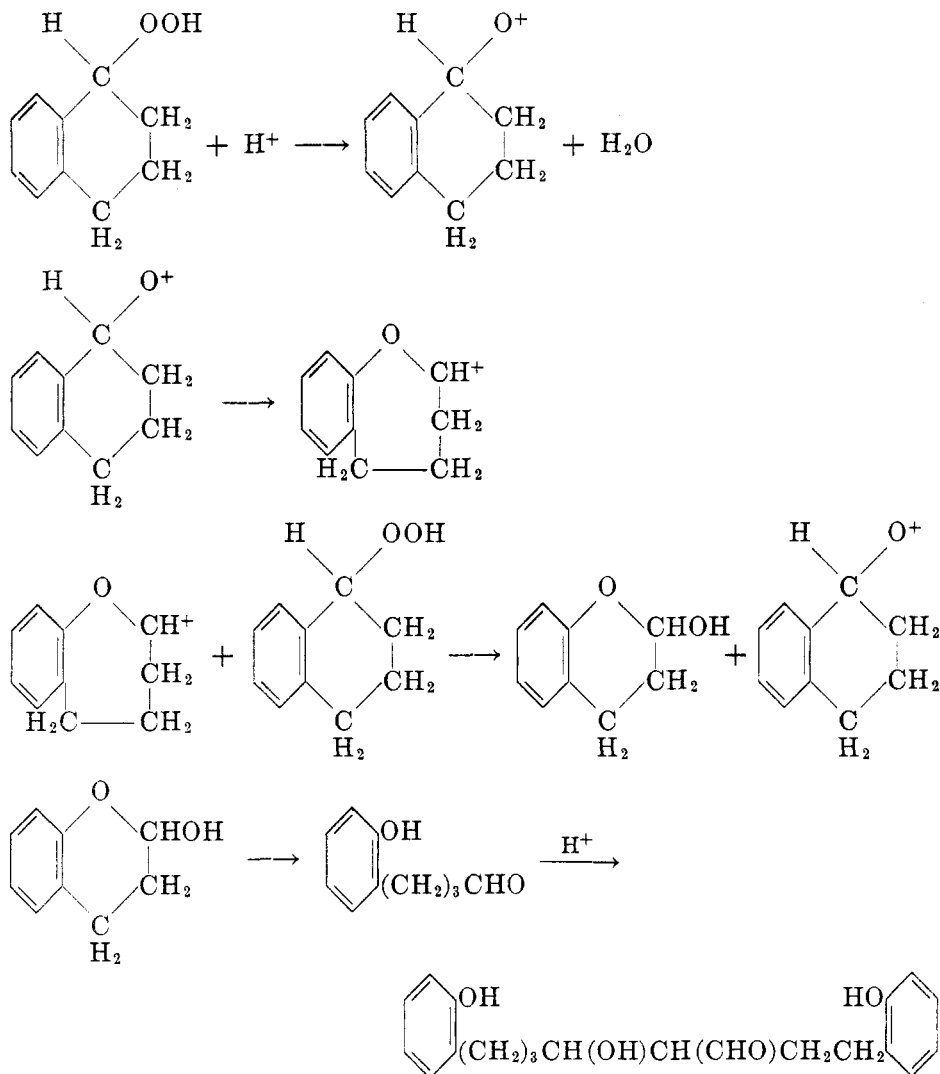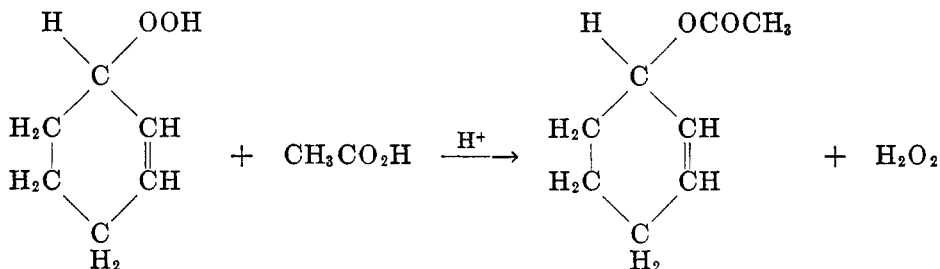

The acetate mixture could not be resolved into pure components. Conceivably, 1-tetralyl hydroperoxide might react metathetically with acetic acid to form an acetate which might undergo oxidation and partial further acetylation. 1-Tetralone itself is not acetylated by glacial acetic acid under the reaction conditions imposed.

Acid-catalyzed decomposition of 3-cyclohexenyl hydroperoxide. The catalytic decomposition of 3-cyclohexenyl hydroperoxide was conducted under the same experimental conditions as that of 1-tetralyl hydroperoxide. The major products isolated were cyclopentene-1-carboxaldehyde (*ca.* 39%) and 3-cyclohexenyl acetate (*ca.* 38%); adipaldehyde (hexanedial) was also found (*ca.* 6%).

Adipaldehyde is the predictable initial reaction product; cyclopentene-3-car-boxaldehyde is a natural secondary product.

$$
\underset{\substack{\text{(cyclohexenyl hydroperoxide)}}}{
\begin{array}{c}
H \quad\; OOH \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}}
+ H^+ \longrightarrow
\begin{array}{c}
H \quad\; O^+ \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}
+ H_2O
$$

$$
\begin{array}{c}
H \quad\; O^+ \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}
\longrightarrow
\begin{array}{c}
\quad\; O \\
^+HC \quad CH \\
| \qquad\quad \| \\
H_2C \quad CH \\
| \qquad\quad | \\
H_2C \text{——} CH_2
\end{array}
$$

$$
\begin{array}{c}
H \quad\; OOH \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}
+
\begin{array}{c}
\quad\; O \\
^+HC \quad CH \\
| \qquad\quad \| \\
H_2C \quad CH \\
| \qquad\quad | \\
H_2C \text{——} CH_2
\end{array}
\rightarrow
\begin{array}{c}
H \quad\; O \\
HO\text{—}C \quad CH \\
| \qquad\quad \| \\
H_2C \quad CH \\
| \qquad\quad | \\
H_2C \text{——} CH_2
\end{array}
+
\begin{array}{c}
H \quad\; O^+ \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}
$$

$$
\begin{array}{c}
H \quad\; O \\
HO\text{—}C \quad CH \\
| \qquad\quad \| \\
H_2C \quad CH \\
| \qquad\quad | \\
H_2C \text{——} CH_2
\end{array}
\rightarrow
\begin{array}{c}
\quad\; CHO \\
H_2C \quad CHO \\
| \qquad\quad | \\
H_2C \quad CH_2 \\
\diagdown C \diagup \\
H_2
\end{array}
\rightarrow
\begin{array}{c}
\quad CHO \\
HC\!=\!=\!CH \\
| \qquad\quad | \\
H_2C \quad CH_2 \\
\diagdown C \diagup \\
H_2
\end{array}
$$

3-Cyclohexenyl acetate is probably the product of a metathetical reaction of the original hydroperoxide with acetic acid.

$$
\begin{array}{c}
H \quad\; OOH \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}
+ CH_3CO_2H \xrightarrow{\;H^+\;}
\begin{array}{c}
H \quad\; OCOCH_3 \\
\diagdown C \diagup \\
H_2C \quad CH \\
| \qquad\; \| \\
H_2C \quad CH \\
\diagdown C \diagup \\
H_2
\end{array}
+ H_2O_2
$$

Farmer and Sundralingam (4), who studied the decomposition of 3-cyclohexenyl hydroperoxide by dilute sulfuric acid at 40° reported 1,2,3-trihydroxycyclohexane as the major product, and the formation of a small amount of cyclopentene-1-carboxaldehyde.

These authors have evolved a tentative reaction scheme to account for the formation of the aldehyde but rejected it because it could not be reconciled with the decomposition products of 1,2-dimethyl-3-cyclohexenyl hydroperoxide. They finally resorted to the explanation that cyclopentenyl derivatives are secondary cyclohexene autoxidation products that contaminate even carefully purified hydroperoxide specimens.

It is interesting to note that no triol was found by us as a product of the decomposition with perchloric acid of cyclohexenyl hydroperoxide dissolved in glacial acetic acid.

Hock (5) proposed a reaction scheme to account for both products, but erroneously based it upon a cyclic peroxide formulation of the hydroperoxide.

The acid-catalyzed decomposition of α-p-xylyl hydroperoxide. Conducted under the same experimental conditions as the reactions previously described, the acid-catalyzed decomposition of α-p-xylyl hydroperoxide was relatively very slow. The products identified were p-tolualdehyde (*ca.* 61%), p-cresol (*ca.* 38%), and formaldehyde. p-Cresol and formaldehyde are predictable products on the basis of the reaction mechanism previously proposed (1). The p-tolualdehyde arises from a non-acidic thermal decomposition. Low temperatures should therefore favor the formation of p-cresol. This has been found to be the case (6).
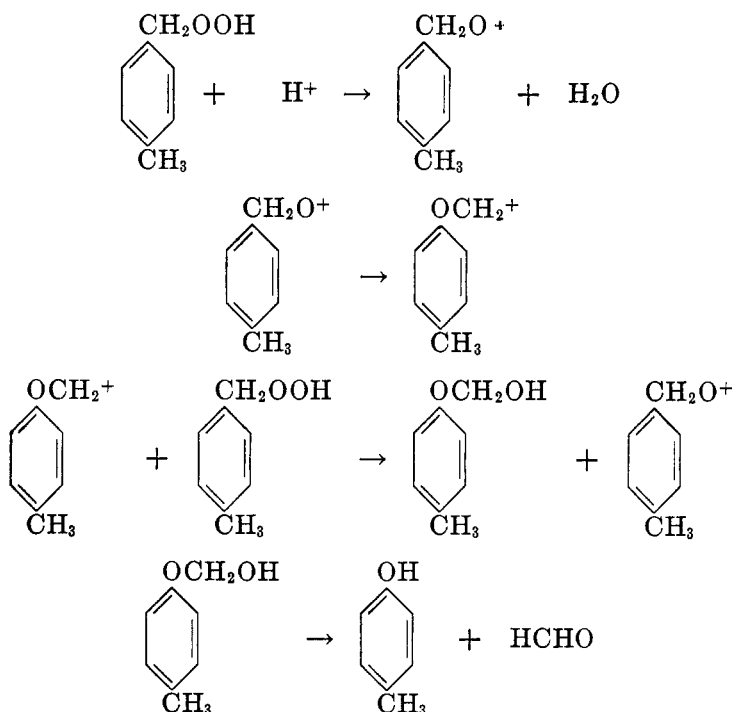
The effect of structure on the acid-catalyzed decomposition of hydroperoxides.
A general theory of acid-catalyzed decomposition of hydroperoxides must include the influence of structure on the susceptibility toward cleavage by acids, not only of the oxygen-to-oxygen bond, but also of the carbon-to-oxygen bond. For purposes of discussion, it is convenient to formulate a general structure of hydroperoxides as $RR'R''C \overset{a}{-} O \overset{b}{-} OH$. The nature of the groups R, R', and R'' might be expected to influence the acid cleavage of bonds a and b, and in fact a wide variation in the behavior of the two bonds has been noted.

The influence of structure on the susceptibility toward acid-cleavage of bond a may be easily predicted using empirical methods in organic chemistry (7):

$$H^+ + RR'R''COOH \rightleftharpoons HOOH + RR'R''C^+$$
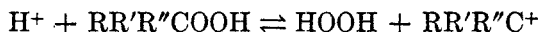
A secondary equilibrium exists between the hydroperoxides, the carbonium ion, and the peroxide.

$$RR'R''COOH + RR'R''C^+ \rightleftharpoons (RR'R''CO)_2 + H^+$$
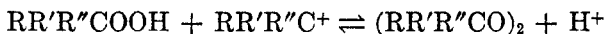
From the data available it may be concluded, at least tentatively, that in general the susceptibility of hydroperoxides toward acid-cleavage of the oxygen-to-oxygen bond (b) parallels the facility with which the hydroperoxides are formed by autoxidation of the corresponding hydrocarbons. It might thus be anticipated that increased substitution of "activating" groups for R, R' and R'' would progressively weaken the bond b with respect to electrophilic attack.

1. $RR'R''COOH + H^+ \rightarrow [RR'R''CO]^+ + HOH$
2. $[RR'R''CO]^+ \rightarrow [R'R''(RO)C]^+$
3. $[R'R''(RO)C]^+ + RR'R''COOH \rightarrow R'R''CO + ROH + [RR'R''CO]^+$

In order that the rearrangement postulated in equation 2 of the reaction sequence may take place readily it would appear that at least one of the groups R, R', R'' be an aromatic group (or the equivalent in activating influence). *tert*-Butyl hydroperoxide does not undergo the necessary rearrangement, and is relatively stable in the presence of acids. In view of the success in preparing *tert*-alkyl hydroperoxides in strongly acid media, stability toward acids would appear to be a general characteristic of this class of compounds. In the absence of activating groups, cyclic olefins react to yield 1,2-glycols.

Relative migratory aptitudes of substituent groups. In consideration of the postulated rearrangement in equation 2 the question arises as to which of the three transitions suggested as possible by a generalized formulation will actually occur:

$$RR'R''CO^+ \begin{array}{l} \nearrow R'R''(RO)C^+ \\ \rightarrow RR''(R'O)C^+ \\ \searrow RR'(R''O)C^+ \end{array}$$
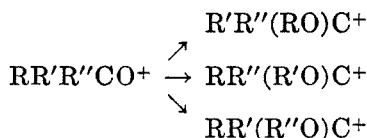
Results of a concurrent study in this laboratory (8) supplemented by those of the present study, indicate that group migratory aptitude is directly related to

group electronegativity (7). Aryl group migration always takes place to the total exclusion of alkyl group migration. In the only case afforded by this study where it is possible to compare the relative migration aptitudes of unlike aryl groups, migration of the supposedly more electronegative o-methoxyphenyl group predominates over migration of the phenyl group.

The analogy between this rearrangement and that of the pinacols (or, indeed, that of any 1,2-ionic shift) is fairly obvious. It is of especial interest that the steric effect, which seems the only logical explanation of the displacement of the

TABLE I

THE PERCHLORIC ACID-CATALYZED INTERACTION OF TERTIARY ALCOHOLS (OR CORRESPONDING OLEFINS) AND HYDROGEN PEROXIDE (OR HYDROPEROXIDES) IN ACETIC ACID SOLUTION

ALCOHOL (OR OLEFIN)	HYDROPEROXIDE	PRODUCT(S) (YIELD, %)
$(CH_2)_5C(OH)C_6H_5$	H_2O_2	C_6H_5OH (97), $(CH_2)_5CO$ (97)
$(CH_2)_5C(OH)C_6H_4$-4-OCH_3	H_2O_2	4-$CH_3OC_6H_4OH$ (90), $(CH_2)_5CO$ (98)
$[(CH_2)_5CH]C(C_6H_5)_2OH$	H_2O_2	C_6H_5OH (87), $(CH_2)_5CHCOC_6H_5$ (92)
$CH_3(n\text{-}C_3H_7)(C_6H_5)COH$	H_2O_2	C_6H_5OH (44), CH_3CO-n-C_3H_7 (31)
$C_6H_5CH_2(C_6H_5)_2COH$	H_2O_2	C_6H_5OH (47), $C_6H_5COCH_2C_6H_5$ (40)
$C_6H_5CH_2CH_2(C_6H_5)_2COH$	H_2O_2	C_6H_5OH (93), $C_6H_5COCH_2CH_2C_6H_5$ (93)
$(CH_2)_5CHOH$	H_2O_2	No reaction
$(CH_2)_5C(OH)CH(CH_2)_5$	H_2O_2	No reaction
Cyclohexene	H_2O_2	Hexahydropyrocatechol (88)
1-Methylcyclohexene	H_2O_2	1-Methyl-2-acetoxycyclohexanol (82)
1-Tetralol	$(CH_3)_3COOH$	$(CH_3)_3COH$, aldol[a] (71)
$(C_6H_5)_3COH$	$(CH_2)_5C(OH)OOH$	C_6H_5OH (83), $(C_6H_5)_2CO$ (84), $(CH_2)_5CO$ (95), $[(C_6H_5)_2CO$—$]_2$ (20)
2-$CH_3OC_6H_4(C_6H_5)_2COH$	$(CH_2)_5C(OH)OOH$	C_6H_5OH (24), $C_6H_5COC_6H_4$-2-OCH_3 (24), 2-$CH_3OC_6H_4OH$ (67), $(C_6H_5)_2CO$ (67), $(CH_2)_5CO$ (91).

[a] The aldol condensation product of γ-o-hydroxybutyraldehyde.

o-methoxyphenyl group in the "pinacol rearrangement series", is considerably less potent in this rearrangement, since the o-methoxyphenyl group rearranges preferentially to a phenyl group.

The method employed in this study, namely the use of an aralkyl alcohol, hydrogen peroxide, and a strong acid (see Table I), is therefore readily adaptable to a general study of the relative migration aptitudes of aryl groups. For this purpose it has two decided practical advantages over pinacol rearrangement studies: (a) the relative ease of preparation of the starting materials (carbinols, as compared with pinacols), and (b) the relative ease of isolation and identification of significant products (phenols and ketones, as compared with pinacolones).

Modification of the described method of study of radical rearrangements, by substitution of a relatively acid-stable hydroperoxide for hydrogen peroxide (Table I) leads to the formation of unsymmetrical peroxides which are also subject to acid cleavage:

$$\text{ROOR}' \xrightarrow{\text{H}^+} \text{ROH} + \text{R}'\text{O}^+ \text{ or } \text{R}'\text{OH} + \text{RO}^+$$
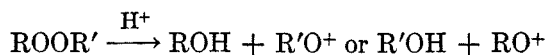
The cleavage products are predictable upon the basis of the relative electro-negativities of the radicals R and R'. The carbinol formed is predominantly or exclusively that derived from the less electronegative radical.

EXPERIMENTAL DETAILS

REAGENTS

Tetralin, cyclohexene, p-xylene. The Eastman Kodak products were carefully fractionated.

1-Hydroxycyclohexyl hydroperoxide. The hydroperoxide, as supplied by courtesy of the Union Bay State Company, m.p. 76–78°, was deemed pure enough.

tert-Butyl hydroperoxide. The product of the Union Bay State Company was refluxed at 40° under an aspirator vacuum for five days, during which time most of the alcoholic impurity was lost, and the peroxide titre with potassium iodide and thiosulfate rose from 73 to 94% of the calculated value. The purified peroxide was stored under nitrogen in the dark, in the refrigerator.

1-Tetralol and 1,2-dihydronaphthalene. Tetralone, b.p. 120–122° (9 mm.), n_D^{20} 1.5704, obtained by tetralin oxidation (9), was reduced with lithium aluminum hydride, and the tetralol was distilled; b.p. 89° (1 mm.); n_D^{20} 1.5642 (yield, 79%). A small portion was heated to 110° with potassium hydrogen sulfate to give 1,2-dihydronaphthalene; b.p. 70–72° (1 mm.); n_D^{20} 1.5820.

Triphenylcarbinol. The carbinol was recrystallized from ethyl alcohol and from benzene until only trace precipitates were observed with 2,4-dinitrophenylhydrazine.

Tertiary alcohols. A series of tertiary alcohols were prepared by the action of an appropriate Grignard reagent and the appropriate ketone: 1-phenylcyclohexanol, m.p. 61°; 1-(p-methoxyphenyl)cyclohexanol, b.p. 90–92°; 1,1,2-triphenylethanol, m.p. 87–89°; 1,1,3-triphenyl-1-propanol, m.p. 86–88°; diphenylcyclohexylcarbinol, m.p. 70–72°; o-methoxy-triphenylcarbinol, m.p. 175°; 2-phenyl-2-pentanol, b.p. 63–66°; 1-cyclohexylcyclohexanol, m.p. 69°.

PREPARATION OF THE HYDROPEROXIDES

Quantitative determination of hydroperoxides. According to a modification of the method of Kokatnur and Jelling (10), a weighed sample of the hydroperoxide (0.1–0.2 g.) was dissolved in 25 ml. of isopropyl alcohol; 1 ml. of glacial acetic acid and 1 ml. of saturated potassium iodide solution were added. The mixture was refluxed for five minutes on the steam-bath in an atmosphere of nitrogen and then allowed to stand in the dark for 15 minutes. The iodine liberated was titrated with 0.1 N standard thiosulfate solution to the disappearance of the iodine color.

1-Tetralyl hydroperoxide. Tetralin (610 g., 4.6 moles) was placed in an irradiation apparatus equipped with an internal-spiral mercury lamp, and a finely divided stream of air was forced through the mixture at 70° for 48 hours. The yellow mixture was transferred to a flask and distilled at a bath temperature not exceeding 65°. Pure tetralin distilled at 35–45° (0.1–0.2 mm.), leaving a viscous yellow oil that was placed in the refrigerator overnight. The solidified mass was broken up and filtered to give faintly yellow crystals of the hydroperoxide which, when crystallized three times from low-boiling ligroin, melted at 56°.

The yield was 130 g.; 60% on the basis of the tetralin used. The white crystals when stored in a dark bottle under nitrogen were stable for several months. The iodide titre was from 95 to 98% of the theoretical.

3-Cyclohexenyl hydroperoxide. Cyclohexene (654 g., 8 moles) was placed in an apparatus equipped with a quartz-spiral mercury vapor lamp, and oxygen was passed through it in a finely divided stream at room temperature for four hours. Some cooling is necessary to offset heat from the light source. The unchanged cyclohexene was distilled at room temperature into a receiver cooled with Dry Ice, leaving a faintly yellow residue (160 g.) which was fractionated at reduced pressure. The portion boiling at 39–40° (0.20 mm.), n_D^{20} 1.4899, was practically pure 3-cyclohexenyl hydroperoxide. The yield was 129 g.; 81% on the basis of the cyclohexene used.

α-p-Xylyl hydroperoxide. p-Xylene (480 g., 4.5 moles) was irradiated for 150 hours at 60° while a stream of dry air was passed through it. According to the method of Hock and Lang (11) the mixture was then chilled to 10°, and 10 g. of an ice-cold 25% sodium hydroxide solution was added slowly with violent stirring. After overnight standing at 0° the sodium salt was washed twice with alcohol-ether. The white plates on drying weighed 8.2 g. The salt was suspended in 50 ml. of ether and carefully neutralized with cold 2 N hydrochloric acid, with sufficient agitation to insure the solution of all free peroxide in the ether layer. The ether layer was then separated, washed with 10% sodium carbonate solution to remove the brown-colored acids, dried, and evaporated. The nearly colorless oil was distilled at mercury-vapor pump pressures on a vacuum line to give 7.2 g., (0.052 mole, 1.2%) of an oily hydroperoxide, n_D^{20} 1.5328. The titre was 91% of the calculated value.

THE ACID-CATALYZED DECOMPOSITION OF HYDROPEROXIDES

1-Tetralyl hydroperoxide. 1-Tetralyl hydroperoxide (82.0 g., 0.5 mole) was dissolved in 300 g. (286 ml., 5.0 moles) of glacial acetic acid. Approximately 0.07 g. (0.0005 mole) of 70% perchloric acid, dissolved in 5 ml. of acetic acid, was added dropwise with vigorous stirring over a period of 30 minutes and with sufficient cooling to keep the temperature between 25° and 30°. After two hours the reaction mixture no longer gave a positive peroxide test with potassium iodide. With continued stirring 1 g. of finely powdered potassium acetate was added. After 15 minutes the potassium perchlorate which separated was removed and the filtrate was concentrated to one-half its volume under reduced pressure at room temperature. The mixture was then flooded with six times its volume of water, neutralized with sodium bicarbonate, and ether-extracted. The ether layer was washed with sodium carbonate solution and then treated with successive 50-ml. portions of 5% sodium hydroxide solution until the aqueous layer was colorless. The ethereal solution was then washed once with water, dried with sodium sulfate, and the ether was removed.

The basic portions were combined, neutralized with hydrochloric acid, and ether-extracted. The ether extract was dried, and ether was removed by distillation; the remaining brownish mass crystallized on standing.[2] Recrystallized from aqueous methanol, the pure white crystals melted at 105° (57.3 g., 70%). This alkali-soluble compound was identified as the aldol condensation product of γ-(o-hydroxyphenyl)butyraldehyde, *2*-HOC$_6$H$_4$(CH$_2$)$_3$-CH(OH)CH(CHO)CH$_2$CH$_2$C$_6$H$_4$-*2*-OH.

Anal. Calc'd for C$_{20}$H$_{24}$O$_4$: C, 73.14; H, 7.37.

  Found: C, 73.3; H, 7.1.

An active hydrogen determination with lithium aluminum hydride indicated 3.03 active hydrogen atoms per molecule.

The compound formed an orange-colored *2,4-dinitrophenylhydrazone* which, on crystallization from chloroform-methanol, melted with decomposition at 184–185°.
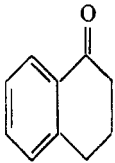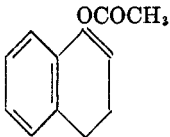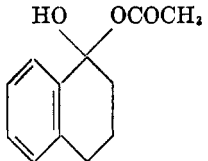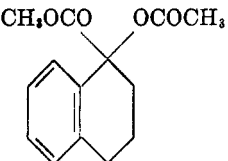
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[2] If the temperature has been allowed to rise above 30° during the reaction, or if separation is incomplete, crystallization is exceedingly difficult to effect even with the aid of pure seed crystals. Furthermore, the isolation of the 2,4-dinitrophenylhydrazone is extremely difficult when the impure material is used.

Anal. Calc'd for $C_{26}H_{28}N_4O_7$: C, 61.4; H, 5.5; N, 11.0.

Found: C, 61.1; H, 5.7; N, 11.3.

The neutral portion of the acid-decomposition product (21.6 g.) was a pale-yellow oil that resisted crystallization; apparent molecular weight, 204 (cryoscopic, benzene). Attempts to separate the components by molecular distillation failed, for the refractive indices

TABLE II

ANALYTICAL DATA RELEVANT TO THE IDENTIFICATION OF ACID-DECOMPOSITION PRODUCTS OF 1-TETRALYL HYDROPEROXIDE

STRUCTURE	ANALYSIS		MOLECULAR WT.[a]	SAPONIFICATION EQUIVALENT	n_D^{20}
	C	H			
Unknown					
(1)	73.2	7.0	204	184	1.5275
(2)	74.3	6.9	—	192	1.5373
(3)	75.6	8.0	—	206	1.5398
(structure: 1-tetralone, O)	82.2	10.0	146	—	1.5704
(structure: OCOCH₃)	76.5	6.39	188	188	—
(structure: HO OCOCH₃)	70.0	6.80	206	206	—
(structure: CH₃OCO OCOCH₃)	67.8	6.45	248	124	—

[a] Cryoscopic in benzene.

of the fractions varied erratically from n_D^{20} 1.5275 to 1.5478. On long standing, distillation temperature and the viscosity of the combined distillates dropped; the refractive index and saponification equivalent rose. With alcoholic potassium hydroxide, a middle fraction (n_D^{20} 1.5373) gave a saponification equivalent of 189. The saponification residue was 1-tetralone: b.p. 124° (10 mm.), n_D^{20} 1.5703; *semicarbazone* m.p. 216–219°. All the fractions, including the residue, slowly formed the dark-red 2,4-dinitrophenylhydrazone of 1-tetralone in methanol-sulfuric acid. The aggregate yield of the *2,4-dinitrophenylhydrazone* would approximate 75% if the material consisted of substantially pure 1-tetralone.

Anal. Calc'd for $C_{16}H_{14}N_4O_4$: N, 17.2. Found: N, 17.1.

In neutral solution semicarbazone formation, if it occurred, was very slow; the semicarbazone formed in slightly acid solution melted at 217–220°, and admixture with an authentic sample of the semicarbazone of 1-tetralone did not depress the melting point.

Anal. Calc'd for $C_{11}H_{13}N_3O$: N, 20.7. Found: N, 20.1.

In acidic solution the material reacted with phenylhydrazine to form 3,4-dihydro-1,2-benzcarbazole, m.p. 156–157° (12).

The foregoing facts indicate that the material is a mixture of 1-tetralone and one or more of its acetates (see Table II).

3-Cyclohexenyl hydroperoxide. To 3-cyclohexenyl hydroperoxide (28.5 g., 0.25 mole), dissolved in 150 g. (143 ml., 2.5 moles) of glacial acetic acid, 0.18 g. (0.00125 mole, 0.5 mole-%) of 70% perchloric acid in 10 ml. of glacial acetic acid was added dropwise over a period of 30 minutes, with stirring. The reaction mixture was allowed to stand for 36 hours at which time the peroxide titre was zero. The solution was flooded with six times its volume of water, neutralized with sodium bicarbonate, and exhaustively extracted with ether. The ether extracts were combined, washed with 10% sodium bicarbonate solution and dried over sodium sulfate; the ether was removed. The crude product (26.9 g.) was then divided into two equal portions.

One portion was shaken for 24 hours with 50 ml. of a saturated solution of sodium bisulfite in 10% aqueous alcohol. The mixture was extracted with ether, and the aqueous layer, from which only tars could be obtained on sodium carbonate neutralization, was discarded. The ether layer was then evaporated at reduced pressure, and the bisulfite extraction process was repeated four times, at which time no precipitate was obtained from the extracted material with 2,4-dinitrophenylhydrazine. The residue (16.7 g.) was distilled *in vacuo.* After a small forerun (0.4 g.), the principal fraction (12.3 g., 38%) distilled at 50–55° (5 mm.).

Anal. Calc'd for $C_8H_{10}O_2$: C, 68.5; H, 8.6; Sapon. equiv., 140.

Found: C, 68.4; H, 9.0; Sapon. equiv., 142.

Identification of the material as 3-cyclohexenyl acetate was confirmed by preparation of the carbanilic ester of the alcohol, m.p. 106–107° (5).

The brown, viscous distillation residue (4 g.) was not further investigated.

The second portion of the crude reaction product was again divided into two portions. The first gave a 39% yield of the *2,4-dinitrophenylhydrazone* of *cyclopentene-1-carboxaldehyde,* m.p. 210–211°.

Anal. Calc'd for $C_{12}H_{12}N_4O_4$: N, 20.3. Found: N, 20.3.

From the second portion, in neutral solution, a mixture of semicarbazones was obtained. The crude product was leached with hot water from which, upon cooling, crystals of the *semicarbazone* of *adipaldehyde,* m.p. 204–205°, separated.

Anal. Calc'd for $C_8H_{16}N_6O_2$: N, 36.8. Found: N, 36.4.

The residual *semicarbazone* of *cyclopentene-1-carboxaldehyde,* crystallized from ethanol, melted at 208–209°. (The melting range of a mixture of the purified semicarbazones was 188–200°.)

Anal. Calc'd for $C_7H_{11}N_3O$: N, 27.2. Found: N, 27.1.

An attempt at fractional distillation of the aldehyde mixture yielded some cyclopentene-1-carboxaldehyde, b.p. 60–64° (13 mm.), n_D^{20} 1.4869, but polymerization of the still-pot content soon rendered further distillation impossible.

α-p-Xylyl hydroperoxide. The hydroperoxide (4.0 g., 0.029 mole) was decomposed in glacial acetic acid (26 g., 25 ml., 0.44 mole) with 0.1 g. (0.00145 mole, 5 mole-%) of 70% perchloric acid. Separation of the phenolic and neutral portions gave 1.05 g. (38%) of *p*-cresol (*benzoate,* m.p. 68–70°) and 2.10 g. (61%) of *p*-tolualdehyde (*2,4-dinitrophenylhydrazone,* m.p. 231–232°.) The aqueous layer from which the *p*-cresol and *p*-tolualdehyde had been ether-extracted yielded the *dimedone* derivative of *formaldehyde,* m.p., 188°.

1-Tetralyl hydroperoxide in the presence of triphenylcarbinol. Molecular equivalents of hydroperoxide and triphenylcarbinol were dissolved in glacial acetic acid to which 0.1 mole-% of perchloric acid was then added with vigorous stirring. In 15 minutes solution

was complete, but in one hour a precipitate was observed. After 4½ hours, the precipitate was removed; additional product, obtained upon concentration of the filtrate, brought the aggregate yield of *1-tetralyl triphenylmethyl peroxide* (m.p. 96–97°) to approximately 100%.

Anal. Calc'd for $C_{29}H_{26}O_2$: C, 85.7; H, 6.5.

Found: C, 85.8; H, 6.3.

To a glacial acetic acid suspension of 1-tetralyl triphenylmethyl peroxide a 70% solution of perchloric acid was added dropwise until the yellow color of the free ion $[(C_6H_5)_3C^+]$ persisted briefly. The mixture was then warmed to homogeneity on the steam-bath (*ca.* five minutes). The precipitate which subsequently formed was identified as *triphenylmethyl peroxide* (33% yield).

The remaining solution was treated in the manner previously described for the 1-tetralyl hydroperoxide acid-decomposition mixture. A 71% yield of the aldol of γ-*o*-hydroxyphenyl-butyraldehyde was thus obtained.

Save that the presence of triphenylcarbinol was established, other products of the reaction were not investigated.

Reactions of tertiary alcohols with hydrogen peroxide in the presence of strong acids, and decomposition of resultant hydroperoxides. To one molecular equivalent of tertiary alcohol was added 1.1 molecular equivalent of 30% hydrogen peroxide and sufficient glacial acetic acid to form a homogeneous mixture. The further addition of 0.1 to 1.0 mole-% of 70% perchloric acid initiated an exothermic reaction which was controlled by cooling; the temperature was not permitted to exceed 40°. The reaction mixture was usually allowed to stand overnight and was then processed in the manner described for the 1-tetralyl hydroperoxide acid-decomposition mixture.

SUMMARY

1. The products formed in the acid-catalyzed decompositions of 1-tetralyl, 3-cyclohexenyl, and α-*p*-xylyl hydroperoxides have been investigated and are shown to be other than those previously reported.

2. A reaction mechanism to elucidate the acid-catalyzed decompositions of hydroperoxides is suggested.

3. A simple general method for the study of the relative migratory aptitudes of aryl groups has been evolved.

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