CLEAVAGES AND REARRANGEMENTS INVOLVING OXYGEN RADICALS AND CATIONS

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CONTENTS

I. INTRODUCTION

In the decomposition of organic peroxides, rupture of the bond between the two peroxidic oxygens is often accompanied by cleavage of an adjacent carbon-to-carbon bond. Such cleavage is not an unusual feature of reactions involving oxygen radicals or oxygen cations. This generalization, which is supported by numerous examples, is a very useful one, casting light on the mechanisms of a number of reactions.

The reactions to be discussed can be formulated as involving either oxygen cations or oxygen free-radicals. A choice between the two mechanisms can often be made on the basis of the reaction conditions, the catalysts, and the products of the reaction. When there is more than one carbon-to-carbon bond next to the unsaturated oxygen, the bond that breaks furnishes a clue to the state of the oxygen. Thus, if the oxygen bears a positive charge, the bond that breaks preferentially is the one leading to that group which would migrate preferentially within a carbonium ion. If the oxygen bears an odd electron instead of a positive charge, the order of bond cleavage is different.

II. PEROXIDE DECOMPOSITION

A. Diacyl peroxides

The decarboxylation of diacyl peroxides is an example of the type of cleavage under consideration, and in most cases is of the free-radical type. When a diaroyl peroxide decomposes in an aromatic solvent, a diaryl is formed by attack of radicals from the peroxide on the solvent.

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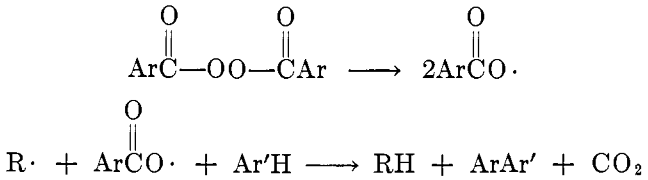


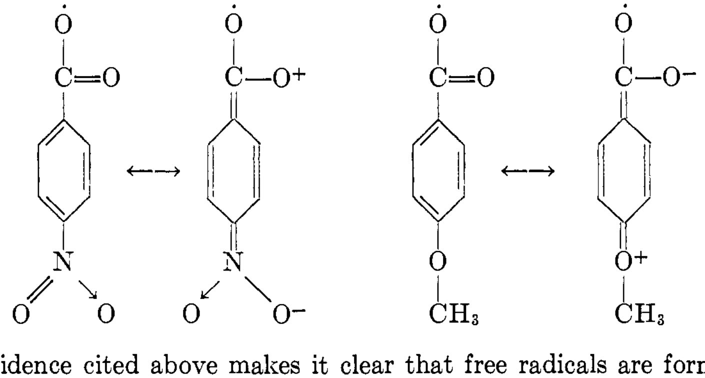
$$\mathrm{Ar\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}Ar \longrightarrow 2Ar\overset{O}{\overset{\|}{C}}O\cdot}$$

$$\mathrm{R\cdot + Ar\overset{O}{\overset{\|}{C}}O\cdot + Ar'H \longrightarrow RH + ArAr' + CO_2}$$

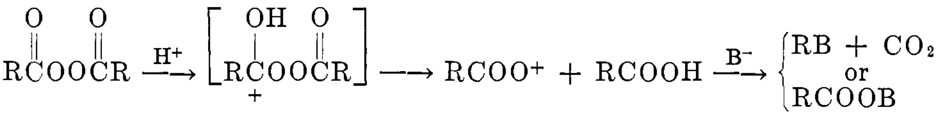
That the attacking fragment is a free radical rather than a positive ion is shown by the invariably ortho- and para-directive effect of various substituents on the solvent nucleus (32, 37, 50, 74). Benzoyl peroxide in nitrobenzene at 74°C. gives *o*- and *p*-nitrodiphenyls (74). Since the nitro group would direct a positive fragment of the peroxide to a meta position, the radical rather than the cationic interpretation is preferred.

Furthermore, the alkoyloxy moiety of an unsymmetrical peroxide in general loses its carbon dioxide more readily than does the aroyloxy part (73, 74). The benzoxy half of an unsymmetrical peroxide in turn loses its carbon dioxide more readily than does a substituted benzoxy moiety; this is true whatever the substituent (73). Such behavior is incompatible with an ionic mechanism but does not clash with the view that free radicals are involved. The substituents tested (73) were phenyl, chloro, methoxy, and nitro, all in the para position. If the mechanism were cationic, it would be reasonable to expect the methoxy group to increase and the nitro group to decrease decarboxylation. Substituents should act as they do on the migration aptitude of groups migrating within a carbonium ion. Positive ions are therefore not intermediate in the decomposition of diacyl peroxides under ordinary conditions.

The free-radical mechanism accounts quite well for the effect of substituents on decarboxylation, as will be seen by inspection of the following stabilizing resonance structures:



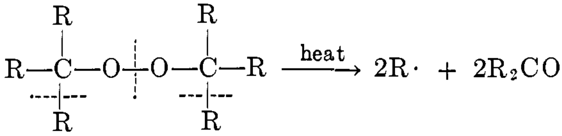
The evidence cited above makes it clear that free radicals are formed when diacyl peroxides decompose in the pure state or in neutral media. But at least two diacyl peroxides, phenylacetyl and benzoyl peroxides, are subject to a general acid catalysis of their decomposition (5). The stronger the acid, the faster is the decomposition induced by it. The acid-catalyzed part of the reaction presumably involves positive ions:



$$\mathrm{R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R} \xrightarrow{H^+} \left[\mathrm{R\underset{+}{\overset{OH}{\overset{|}{C}}}OO\overset{O}{\overset{\|}{C}}R}\right] \longrightarrow \mathrm{RCOO^+} + \mathrm{RCOOH} \xrightarrow{B^-} \begin{cases}\mathrm{RB + CO_2}\\ \text{or}\\ \mathrm{RCOOB}\end{cases}$$

B. Dialkyl peroxides

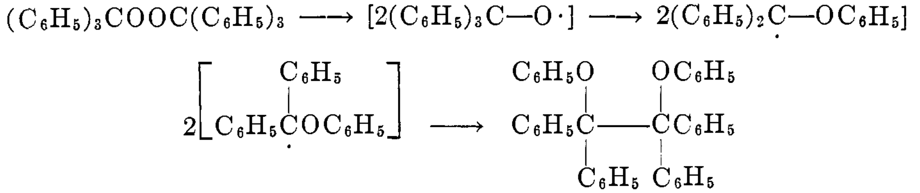
The dialkyl peroxides provide numerous examples of the cleavage of carbon-to-carbon bonds adjacent to the oxygen–oxygen bond. The generality of this reaction for tertiary alkyl peroxides has been pointed out by George and Walsh (33):



$$\mathrm{R{-}\underset{R}{\overset{R}{C}}{-}O{-}O{-}\underset{R}{\overset{R}{C}}{-}R} \xrightarrow{\text{heat}} 2\mathrm{R\cdot} + 2\mathrm{R_2CO}$$

$$2\mathrm{R\cdot} \longrightarrow \mathrm{RR}$$

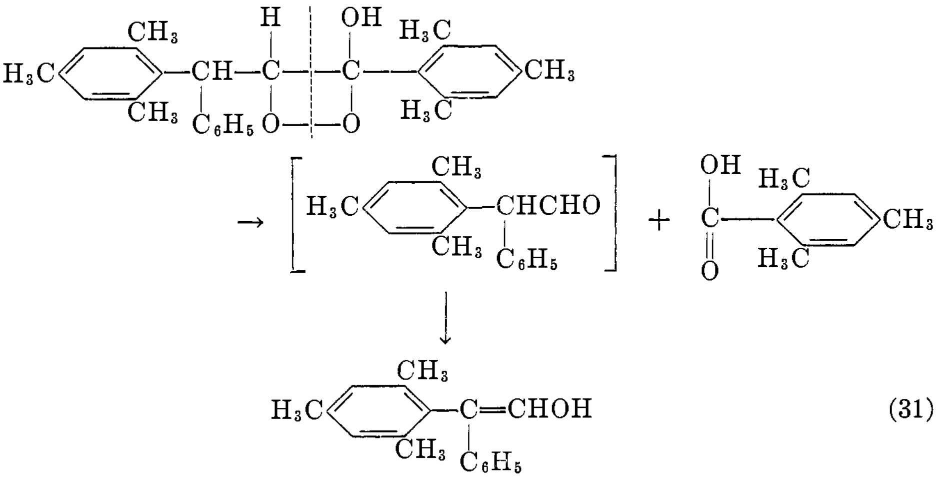
Twelve examples are given in table 1; most of them are vapor-phase reactions and hence free-radical rather than ionic. They fit the scheme given above or a variant of it. In the case of Wieland's triphenylmethyl peroxide (reaction 7 of table 1), the driving force seems to be resonance stabilization of a free radical rather than carbonyl formation.



$$\mathrm{(C_6H_5)_3COOC(C_6H_5)_3 \longrightarrow [2(C_6H_5)_3C{-}O\cdot] \longrightarrow 2(C_6H_5)_2\underset{\cdot}{C}{-}OC_6H_5]}$$

$$2\left[\mathrm{C_6H_5\underset{\cdot}{\overset{C_6H_5}{C}}OC_6H_5}\right] \longrightarrow \mathrm{C_6H_5\overset{C_6H_5O}{\underset{C_6H_5}{C}}{-}\overset{OC_6H_5}{\underset{C_6H_5}{C}}C_6H_5}$$

In the cyclic enol peroxides (reactions 9–12) only one carbon bond breaks; it is adjacent to both of the peroxide oxygens.



(31)

TABLE 1

Decomposition of alkyl peroxides

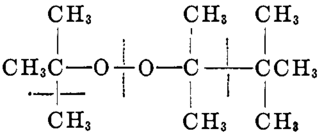
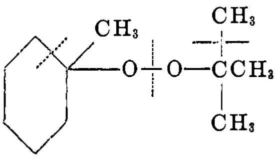
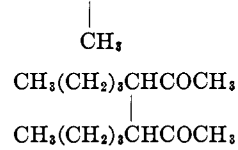
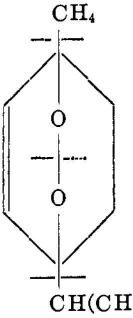
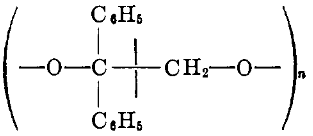
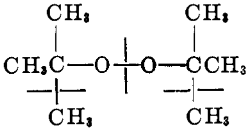
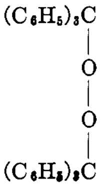
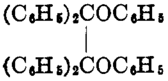
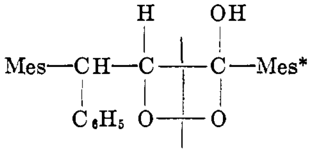
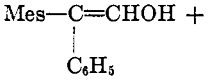
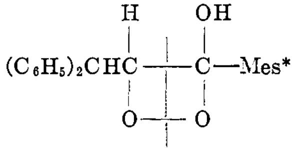
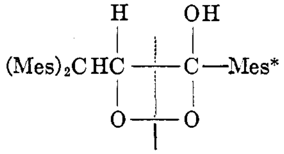
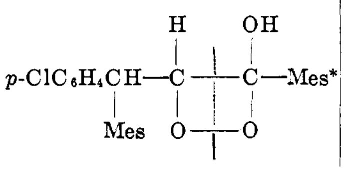
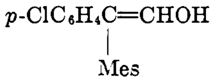
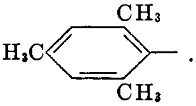
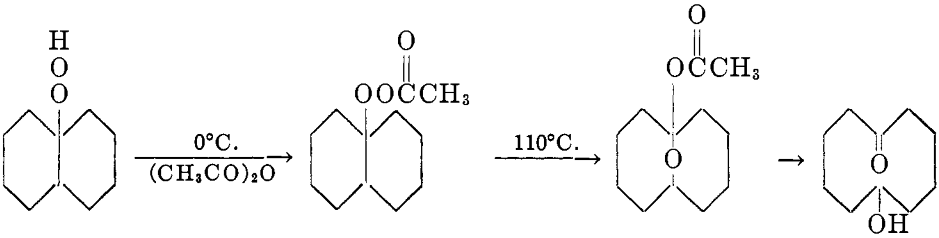
NO.	PEROXIDE	CONDITIONS	PRODUCTS	REFERENCE
1...	$(C_2H_5)_3COOC(C_2H_5)_3$	250°C., glass wool	$C_2H_5COC_2H_5 + n\text{-}C_4H_{10}$	(46)
2...	 $CH_3\overset{CH_3}{\underset{CH_3}{C}}—O—O—\overset{CH_3}{\underset{CH_3}{C}}—\overset{CH_3}{\underset{CH_3}{C}}CH_3$	250°C., glass wool	$CH_3COCH_3 + (CH_3)_4C$	(46)
3...		250°C., glass wool	$C_2H_6 + CH_3COCH_3 +$  $CH_3(CH_2)_3\underset{CH_3}{CH}COCH_3 +$ $\underset{CH_3(CH_2)_3CHCOCH_3}{CH_3(CH_2)_3CHCOCH_3}$	(46)
4...		Distil in nitrogen	$C_2H_6 + C_3H_6 +$ $CH_3CH{=}CH_2$	(40)
5...	 $\left(—O—\overset{C_6H_5}{\underset{C_6H_5}{C}}—CH_2—O—\right)_n$	H_2O, 120–130°C.	$C_6H_5COC_6H_5 + HCHO$	(60)
6...	 $CH_3\overset{CH_3}{\underset{CH_3}{C}}—O—O—\overset{CH_3}{\underset{CH_3}{C}}CH_3$	Vapor	$CH_3COCH_3 + C_2H_6$	(33)
7...	 $(C_6H_5)_3C—O—O—C(C_6H_5)_3$	Boiling xylene	 $(C_6H_5)_2COC_6H_5$ $(C_6H_5)_2COC_6H_5$	(71)

TABLE 1—*Concluded*

NO.	PEROXIDE	CONDITIONS	PRODUCTS	REFERENCE
8...	$CH_3CH_2CH_2O$ | $CH_3CH_2CH_2O$	230°C.	$CH_3CH_2CH_2CH_3$ + HCHO	(34)
9...		Melt	 $Mes\text{—}\underset{C_6H_5}{C}\text{=}CHOH$ + MesCOOH	(31)
10...		Melt	$(C_6H_5)_2CHCHO$ + MesCOOH	(44)
11...		Melt	$(Mes)_2C\text{=}CHOH$ + MesCOOH	(31)
12...		Melt	 $p\text{-}ClC_6H_4\underset{Mes}{C}\text{=}CHOH$	(31)

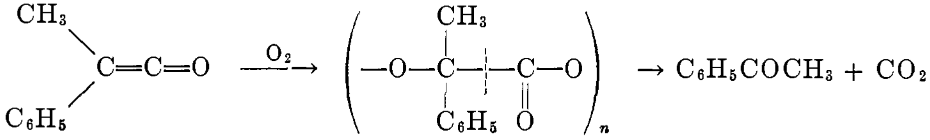
* Mes = 

An interesting application and an unusual example of the peroxide cleavage reaction has been reported by Criegee (16):



This is analogous to the rearrangement of triphenylmethyl peroxide.

Another variation is the decomposition of ketene peroxides, for example (62):



C. Hydroperoxides

Like the dialkyl peroxides, the hydroperoxides tend to cleave at the α-carbon atom. A few such reactions are summarized in table 2. The course of the reactions numbered 3, 4, and 5 may not be immediately obvious, on account of the further

TABLE 2

Decomposition of alkyl hydroperoxides

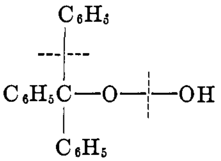
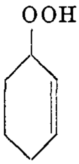
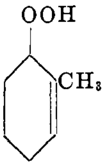
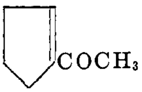
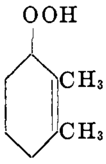
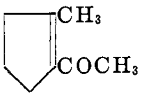
NO.	PEROXIDE	CONDITIONS	PERTINENT PRODUCTS	REFERENCE
1	CH_3CH_2OOH	Sealed tube, 100°C.	HCHO	(34)
2	 $\underset{C_6H_5}{\overset{C_6H_5}{C_6H_5C}}-O-OH$	Melt	$C_6H_5COC_6H_5$ + C_6H_5OH	(72)
3		Dilute H_2SO_4		(25, 38)
4		Dilute H_2SO_4		(25)
5		Dilute H_2SO_4		(25)
6	$(CH_3)_3COOH$	Vapor phase	CH_3COCH_3	(33)
7	$CH_3CH_2CH_2OOH$	Glass wool, heat	CH_3CH_3 + HCHO	(34)

TABLE 3

The reactions of carbonium ions with hydrogen peroxide

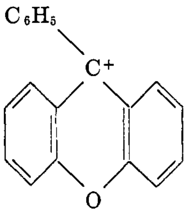
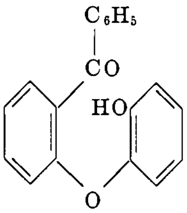
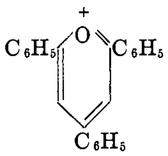
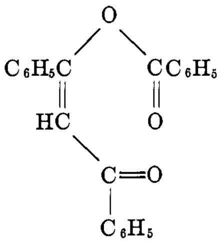
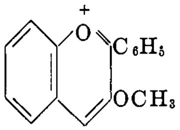
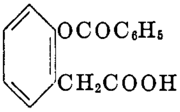
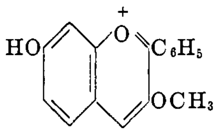
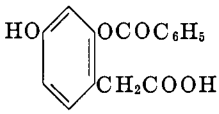
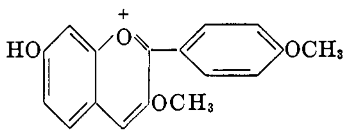
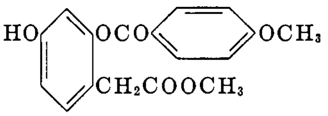
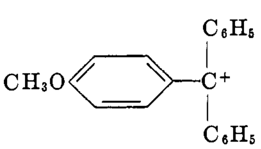
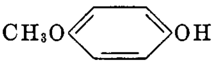
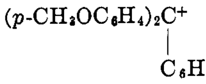
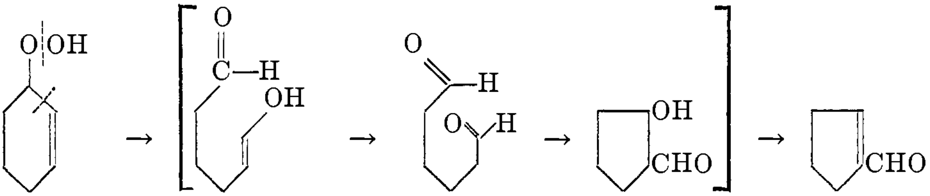
NO.	CARBONIUM ION	PRODUCT	REFERENCE
1...			(54)
2...			(22)
3...			(20)
4...			(20)
5...	 (picrate)		(20)
6...		 + $C_6H_5COC_6H_5$	(23)
7...	 $(p\text{-}CH_3OC_6H_4)_2C^+-C_6H_5$	p-$CH_3OC_6H_4OH$ + p-$CH_3OC_6H_4COC_6H_5$	(23)

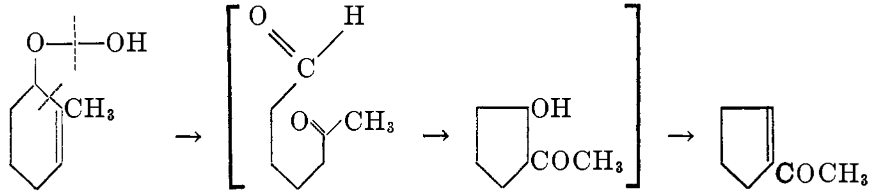
TABLE 3—*Concluded*

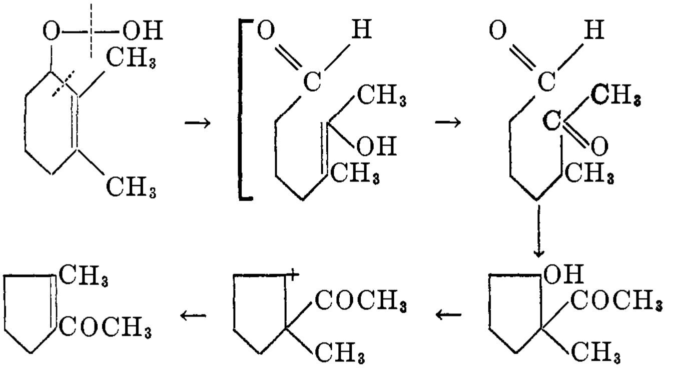
NO.	CARBONIUM ION	PRODUCT	REFERENCE
8. . .	$(p\text{-}CH_3OC_6H_4)_3C^+$	$p\text{-}CH_3OC_6H_4OH$ + $(p\text{-}CH_3OC_6H_4)_2CO$	(23)
9. . .	$(p\text{-}C_6H_5OC_6H_4)_2\underset{\underset{C_6H_5}{\vert}}{C^+}$	$p\text{-}C_6H_5OC_6H_4COC_6H_5$ + $p\text{-}C_6H_5OC_6H_4OH$	(23)
10. . .	$(p\text{-}C_6H_5OC_6H_4)_3C^+$	$(p\text{-}C_6H_5OC_6H_4)_2CO$ + $p\text{-}C_6H_5OC_6H_4OH$	(23)
11. . .	$(p\text{-}O_2NC_6H_4)_3C^+$	$(p\text{-}O_2NC_6H_4)_2CO$ + $p\text{-}O_2NC_6H_4OH$	(23)
12. . .	$p\text{-}O_2NC_6H_4\overset{\overset{C_6H_5}{\vert}}{\underset{\underset{C_6H_5}{\vert}}{C^+}}$	$p\text{-}O_2NC_6H_4COC_6H_5$ + C_6H_5OH	(23)

changes that follow the initial cleavage. The products can be accounted for as follows:

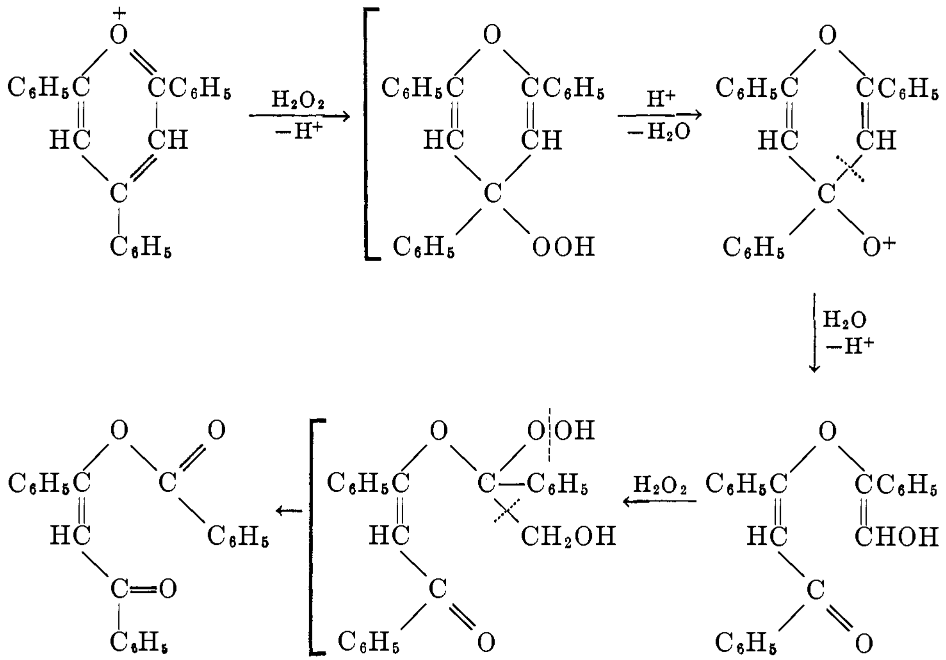


Adipic dialdehyde was isolated in some experiments.





The reactions of carbonium ions with hydrogen peroxide can best be explained as hydroperoxide decompositions. Dilthey and his collaborators have in fact isolated hydroperoxides from carbonium ions in six cases. But usually the product isolated from the reaction of a carbonium ion with hydrogen peroxide is that to be expected from the decomposition of the hydroperoxide, rather than the hydroperoxide itself. A number of such reactions are given in table 3. Let us consider reaction 2 of table 3 as an example:

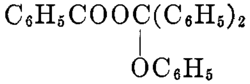


The other reactions listed involve fewer steps.

It will be seen from the reactions of table 3 that the effect of substituents on the course of the reaction favors the oxygen cation interpretation rather than the oxygen radical one. Some of the autoxidations with hydroperoxide intermediates, to be described later, however, follow a course that suggests free-radical intermediates. The present author has made some attempts (unpublished) to induce ionic decomposition of tertiary butyl hydroperoxide with acids; the only effect of acids was to reverse the addition of hydrogen peroxide to isobutylene by which tertiary butyl hydroperoxide is formed. Wieland and Maier report (72) that triphenylmethyl hydroperoxide is stable in acids; the decomposition induced by heat alone is therefore a radical reaction. Acids should catalyze the ionic reaction by the following mechanism:

$$ROOH + H^+ \longrightarrow RO\overset{H}{\underset{+}{O}}H \rightarrow RO^+ + H_2O$$

Wieland and Maier (72) also report that triphenylmethyl peroxide reacts readily with benzoyl chloride to form:

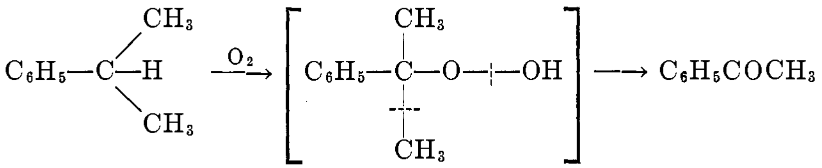


$$C_6H_5COO\underset{\displaystyle |\atop \displaystyle OC_6H_5}{C}(C_6H_5)_2$$

This probably goes by way of the perester.

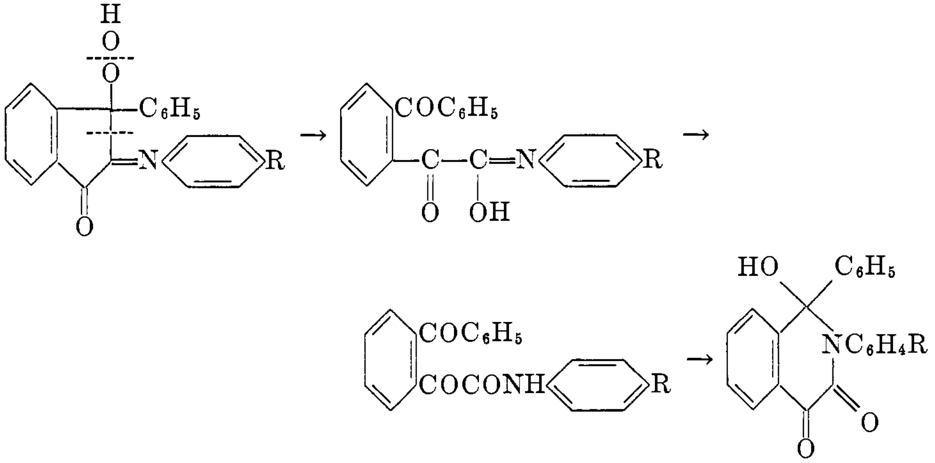
D. *Autoxidation*

Hydroperoxides are sometimes isolated from hydrocarbons exposed to air (25, 38). This, together with the correspondence between the products of autoxidation and the products of hydroperoxide decomposition, makes it seem likely that hydroperoxides are intermediate in the autoxidation reaction (70). A number of reactions susceptible to such an interpretation are listed in table 4. The hydroperoxide is commonly formed at a tertiary carbon or at a carbon atom in the α-position to a double bond. Reaction 1 would thus be formulated as follows:



On the other hand, reaction 3 probably goes by removal of a hydrogen atom to give an alkoxy free radical.

Reaction 8 (of table 4) is more complicated than some of the others. The following hydroperoxide intermediate satisfies both the preference for a tertiary carbon atom and an allylic double bond:



In table 4 there are also listed autoxidations of another kind, in which oxygen is added to a double bond or system of double bonds. Reaction 15, which goes by way of a ketene peroxide, is of this type. The ketene peroxides are very unstable but are sometimes isolated (62).

TABLE 4

Cleavage during autoxidation

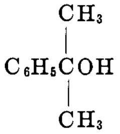
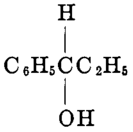
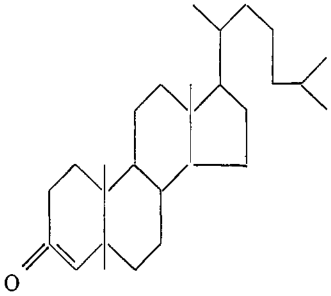
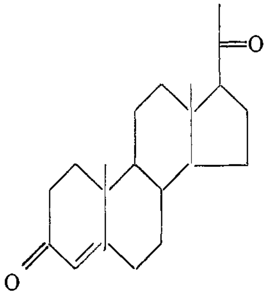
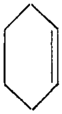
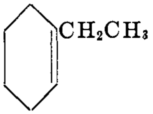
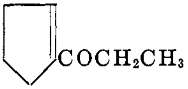
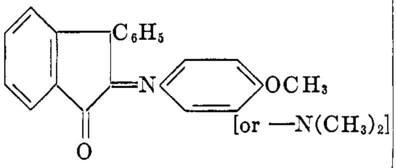
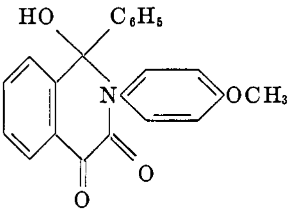
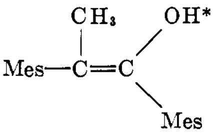
NO.	SUBSTANCE	PRODUCT	REFERENCE
1...	$C_6H_5CH(CH_3)_2$	$C_6H_5COCH_3$	(63)
2...	$p\text{-}CH_3C_6H_4CH(CH_3)_2$	$p\text{-}CH_3C_6H_4COCH_3$	(63)
3...	 $C_6H_5\overset{CH_3}{\underset{CH_3}{C}}OH$	$C_6H_5COCH_3$ (trace)	(64)
4...	 $C_6H_5\overset{H}{\underset{OH}{C}}C_2H_5$	C_6H_5CHO (trace)	(64)
5...			(10)
6...			(51)
7...			(51)
8...			(53)
9...		MesCOCH₃ + MesOH + CO	(29)

TABLE 4—*Continued*

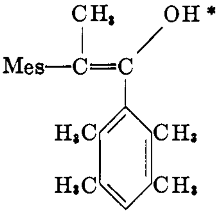
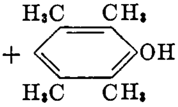
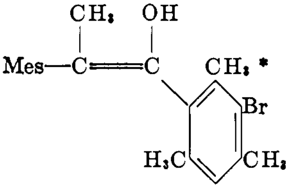
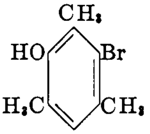
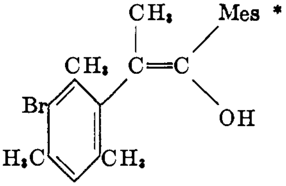
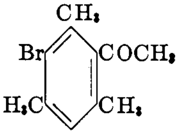
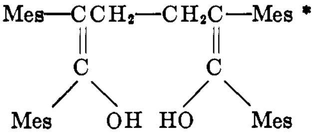
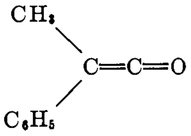
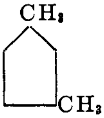
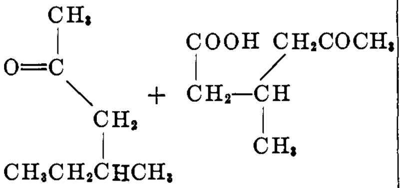
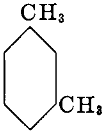
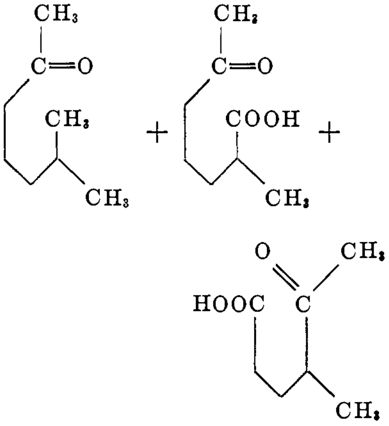
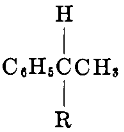
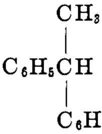
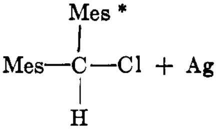
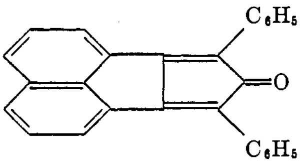
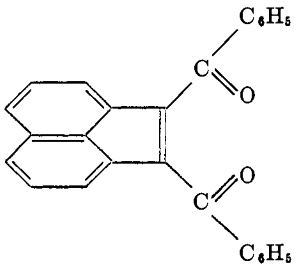
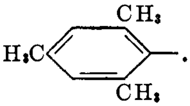
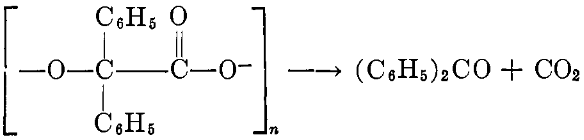
NO.	SUBSTANCE	PRODUCT	REFERENCE
10...		MesCOCH₃ + CO + 	(29)
11...		MesCOCH₃ + 	(30)
12...		 + MesOH	(30)
13...		MesOH + MesCOCH$_2$CH$_2$COMes	(28)
14...		CH$_3$COC$_6$H$_5$ + CO$_2$	(62)
15...	$(C_6H_5)_2C{=}C{=}O$	C$_6$H$_5$COC$_6$H$_5$ + CO$_2$	(62)
16...			(12)

TABLE 4—*Concluded*

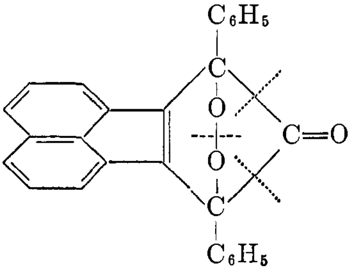
NO.	SUBSTANCE	PRODUCT	REFERENCE
17...			(13)
18...	 $C_6H_5\overset{H}{\underset{R}{C}}CH_3$ (R = ethyl, *n*-propyl, or *n*-butyl)	$C_6H_5COCH_3$	(65)
19...	$(C_6H_5)_3CH$	$C_6H_5COC_6H_5 + C_6H_5OH$	(65)
20...	 $C_6H_5\overset{CH_3}{\underset{C_6H_5}{C}}H$	$C_6H_5COC_6H_5 + HCOOH$	(65)
21...	 $Mes-\overset{Mes^*}{\underset{H}{C}}-Cl + Ag$	MesOH + MesCOOH + $(Mes)_2CO$	(49)
22...		 + CO	(19)

* Mes = 



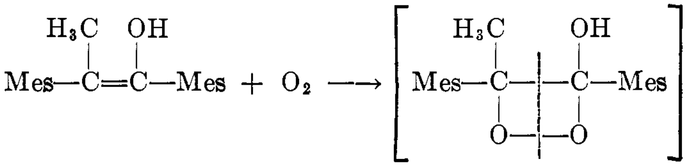
$$\left[-O-\overset{C_6H_5}{\underset{C_6H_5}{C}}-\overset{O}{\overset{\|}{C}}-O^-\right]_n \longrightarrow (C_6H_5)_2CO + CO_2$$

Similarly, reaction 22 may go by way of a 1,4-adduct:



The autoxidation of enols (reactions 9–13) could be formulated in either of two ways:

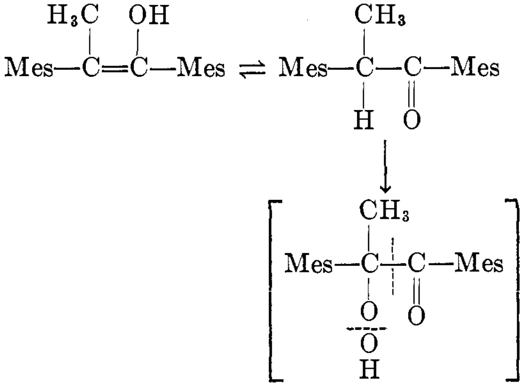
(*a*)



$$\text{Mes}-\overset{H_3C}{C}=\overset{OH}{C}-\text{Mes} + O_2 \longrightarrow \left[\text{Mes}-\overset{H_3C}{\underset{O}{C}}-\overset{OH}{\underset{O}{C}}-\text{Mes}\right]$$

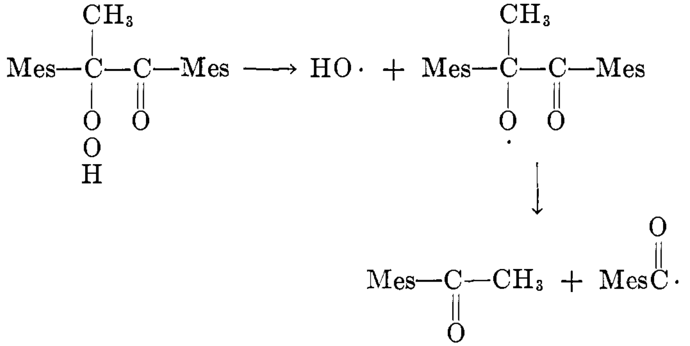
or

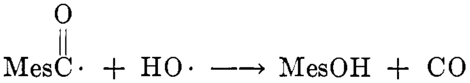
(*b*)



$$\text{Mes}-\overset{H_3C}{C}=\overset{OH}{C}-\text{Mes} \rightleftharpoons \text{Mes}-\overset{CH_3}{\underset{H}{C}}-\underset{O}{\underset{\|}{C}}-\text{Mes}$$

Path (*b*) is greatly to be preferred for reactions 9–13. Although it is true that peroxides like that of path (*a*) have been made by the air oxidation of enols (see reaction 9 of table 1), such peroxides decompose to carboxylic acids. This is to be expected, since the carbon atom of the future carboxyl group already bears a hydroxyl and formation of the carboxylic acid is a one-step process. But in reactions 9–13 of table 4 the product is not a carboxylic acid, but carbon monoxide and a phenol. Such a result is readily explained by path (*b*), since acyl radicals are known to lose carbon monoxide.





$$\mathrm{Mes\overset{\displaystyle O}{\overset{\|}{C}}\cdot + HO\cdot \longrightarrow MesOH + CO}$$

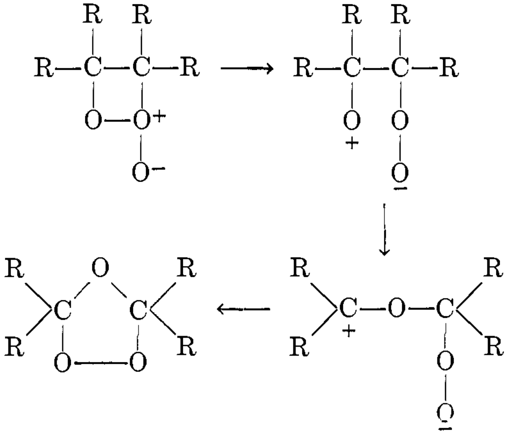
Although some intermediate hydroperoxides decompose by way of oxygen cations (see page 393), it will be seen by inspection of table 4 that the order of bond cleavage in autoxidation often indicates an oxygen free-radical mechanism for the decomposition of the hydroperoxide. For example, in reactions 1, 2, 5, 18, and 20 of table 4, it is the alkyl group that is split off rather than the aryl group.

Whether the decomposition of a given hydroperoxide involves radical or cationic intermediates probably depends on the amount of polarization of the peroxide bond by the other groups attached to the perhydroxylated carbon atom.

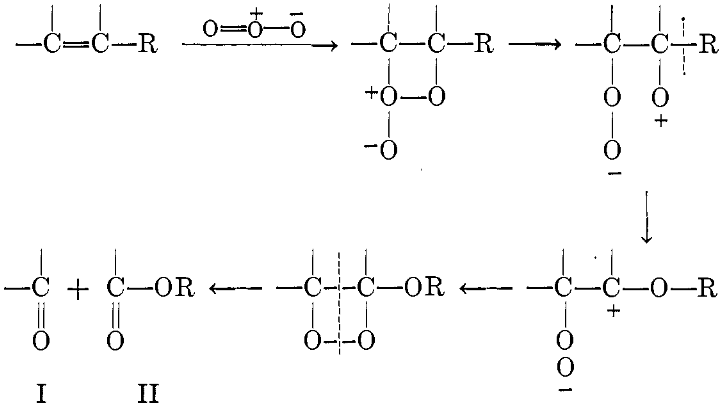
Those reactions of table 3 whose products are those to be expected on the basis of an ionic mechanism all involve compounds containing groups which place a partial negative charge on the alpha carbon atom.

E. Ozonization

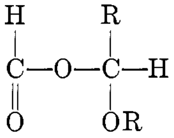
The ozonization of double bonds probably involves the preliminary formation of a "molozonide" (61). But the isolable ozonides appear to have a rearranged, "isozonide" structure. The most plausible mechanism is an ionic one:



Support for the ionic mechanism, aside from the inherent plausibility of ionic cleavage of a bond that bears a polar group on one end, is derived from the occasionally abnormal course of ozonization. When one of the carbon atoms next to the double bond bears an oxygen or nitrogen atom (an electron-donating atom) or when it is part of a benzene ring bearing the sort of substituent that encourages migration within a carbonium ion, oxygen is introduced between the double bond and the carbon atom in question (35, 36, 52, 58, 75). The more electron-donating the substituent, the greater is the proportion of abnormal product. Table 5 contains typical examples of abnormal ozonolysis. All of these deviations from the usual path of ozonolysis can be explained by the mechanism below, in which R is a group of the type suited to migration within a carbonium ion.



The fate of product II is observed to depend on details of its structure not shown. For example, if it is



$$\mathrm{HC({=}O){-}O{-}CH(R)(OR)}$$

it will lose carbon monoxide as the ozonide decomposes. Young *et al.* (75) report that carbon monoxide is evolved spontaneously from the ozonide even below room temperature; this is further evidence of an unusual structure.

As will be seen in the next section of this review, carbonyl compounds are also attacked by ozone and by hydrogen peroxide. Accordingly, if the reaction mixture is wet during the ozonization, part of the abnormal product may come from attack by ozone or by hydrogen peroxide on the hydrolysis products of the normal ozonide. Evidence that the latter is not the principal explanation of abnormal ozonolyses is provided, however, by the isolation of abnormal ozonides (75). Furthermore, the yields of phenols from aldehydes are lower than the yields of phenols from the corresponding cinnamic esters under comparable conditions (58). Hydrogenation rather than hydrolysis of the ozonide does not prevent the formation of abnormal products (69, 75).

III. REACTIONS BETWEEN PEROXIDES AND CARBONYL COMPOUNDS

A. Ozone

In table 6 are gathered some examples of the ozonolysis of carbonyl compounds. Large-ring ketones are ozonized to the corresponding dicarboxylic acids in good

TABLE 5

Abnormal ozonizations

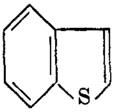
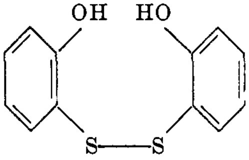
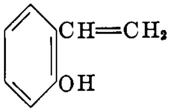
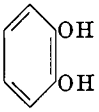
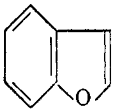
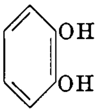
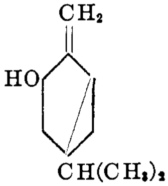
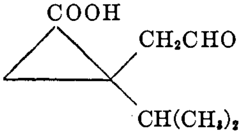
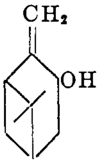
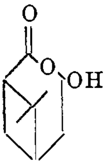
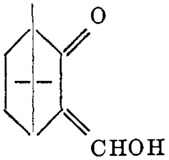
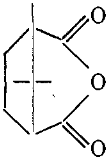
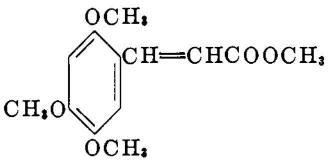
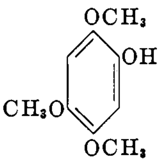
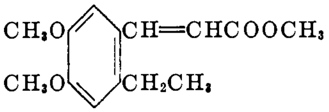
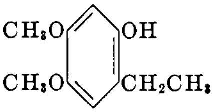
NO.	SUBSTRATE	ABNORMAL PRODUCT	YIELD *per cent*	REFERENCE
1...				(69)
2...			10	(69)
3...			10	(69)
4...				(35)
5...				(36)
6...				(52)
7...			48.2	(58)
8...			46.4	(58)

TABLE 5—*Continued*

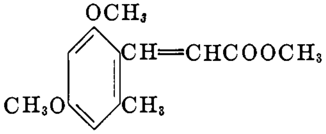
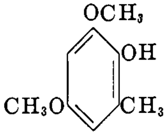
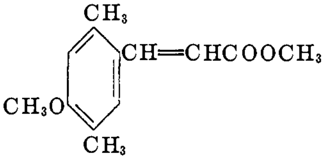
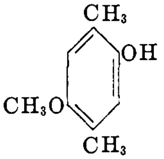
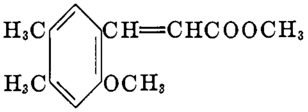
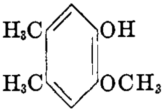
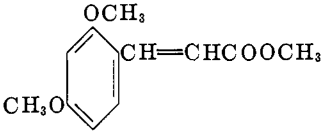
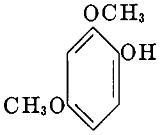
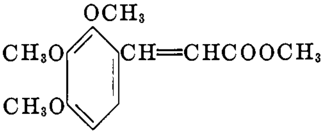
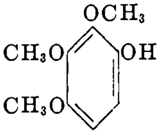
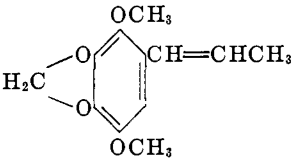
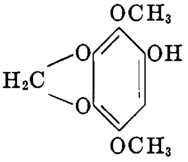
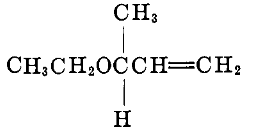
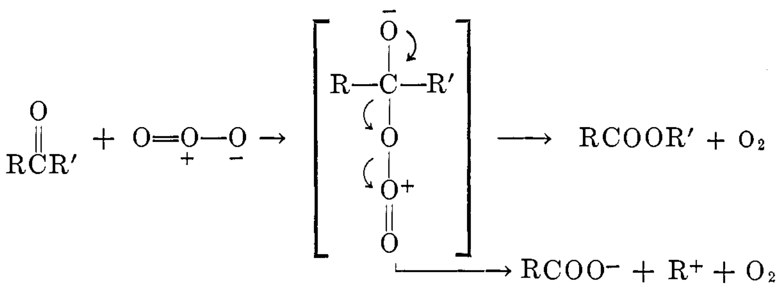
NO.	SUBSTRATE	ABNORMAL PRODUCT	YIELD *per cent*	REFERENCE
9...			27.1	(58)
10...			22.0	(58)
11...			15.9	(58)
12...			15.0	(58)
13...			13.7	(58)
14...			5	(58)
15...	$CH_3CH{=}CHCH_2OC_6H_4NO_2(p)$	$HCOOH$	8*	(75)
16...	$CH_3CH{=}CHCH_2OC_6H_5$	$HCOOH$	15*	(75)
17...	$CH_3CH{=}CHCH_2OH$	$HCOOH$	23*	(75)
18...	$CH_3CHOHCH{=}CH_2$	CH_3COOH	25*	(75)
19...	$CH_3(CH_2)_3CHOHCH{=}CH_2$	$CH_3(CH_2)_3COOH$	38*	(75)
20...	$CH_3(CH_2)_2CHOHCH{=}CHCH_3$	$CH_3(CH_2)_2COOH$	50*	(75)
21...	$CH_3CH_2CHOHCH{=}CHCH_3$	CH_3CH_2COOH	15*	(75)
22...	$C_6H_5CH{=}CHCH_2OH$	$HCOOH$	60*	(75)

TABLE 5—*Concluded*

NO.	SUBSTRATE	ABNORMAL PRODUCT	YIELD	REFERENCE
			per cent	
23...	$CH_3CH{=}CHCH_2OCH_2CH_3$	HCOOH	25*	(75)
24...	 $CH_3CH_2O\overset{CH_3}{\underset{H}{C}}CH{=}CH_2$	CH_3COOH	35*	(75)
25...	$CH_3CH{=}CHCH_2N(C_2H_5)_2$	HCOOH	54*	(75)
26...	$CH_3CH{=}CHCOOH$	HCOOH	5*	(75)
27...	$CH_3CH{=}CHCHO$	HCOOH	10*	(75)
28...	$CH_3CH{=}CHCOCH_2CH_3$	HCOOH	13*	(75)

* Per cent of total acids after treatment with silver oxide.

yield and without undesirable byproducts (66). A mechanism for the reaction with carbonyl compounds might be:



$$R^+ + O_3 \rightarrow RCH_2O^+ + O_2$$
$$\downarrow$$
$$RCHO + H^+ \rightarrow RCOOH$$

An aldehyde (R or R′ is hydrogen) can give either an acid or an ester of formic acid, depending on whether the hydrogen or the other group migrates. Ordinarily, the hydrogen migrates and the product is an acid. But when the alkyl or aryl group is of the sort that migrates within a carbonium ion, a certain amount of phenol or other degraded product is formed. The phenol is produced by way of the formate. Acids, but not the likewise expected esters, are formed with ketones.

A methoxyl group in the meta position does not lead to phenol formation when benzaldehydes are ozonized (68).

B. Hydroperoxides

A number of reagents other than ozone oxidize aldehydes and ketones to the corresponding esters or lactones. Such reagents have in common the perhydroxyl group. Table 7 lists some oxidations of this type; in each case the reagent is hydrogen peroxide, Caro's acid (monopersulfuric acid), peracetic acid, perbenzoic

TABLE 6

Ozonolysis of carbonyl compounds

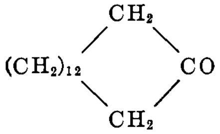
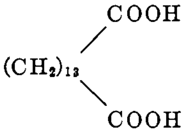
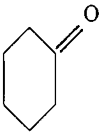
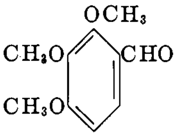
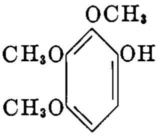
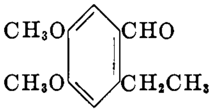
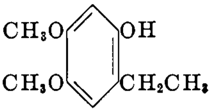
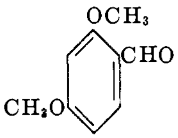
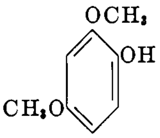
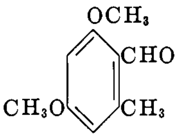
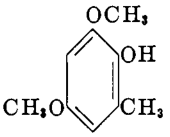
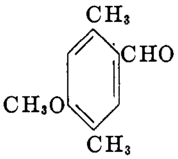
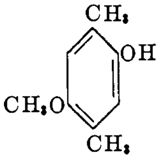
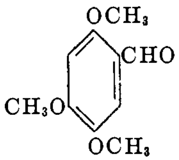
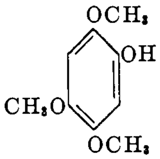
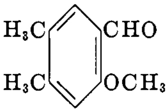
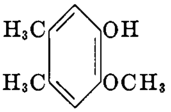
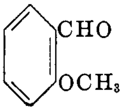
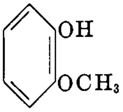
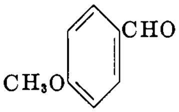
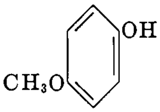
NO.	SUBSTRATE	PRODUCT	YIELD	REFERENCE
			per cent	
1...				(66)
2...		$(CH_2)_4(COOH)_2$		(66)
3...			20.1	(58)
4...			14.5	(58)
5...			14.0	(58)
6...			8.0	(58)
7...			4.4	(58)
8...			4.1	(58)

TABLE 6—*Concluded*

NO.	SUBSTRATE	PRODUCT	YIELD	REFERENCE
			per cent	
9...			3.9	(58)
10...			3	(68)
11...			4	(68)

acid, or perphthalic acid. The reagent, ROOH, evidently adds to the carbonyl double bond:

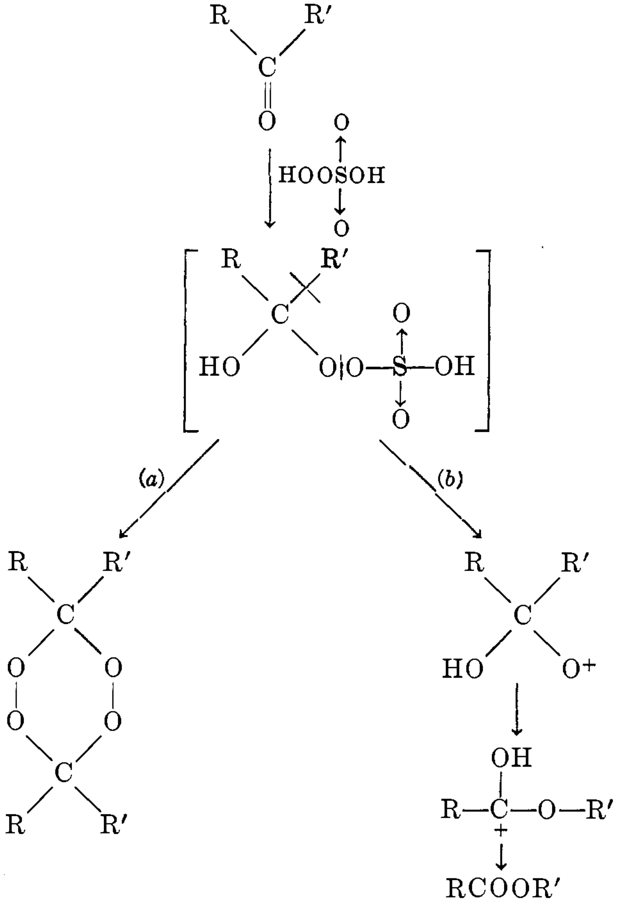


TABLE 7

Reactions of carbonyl compounds with hydroperoxides

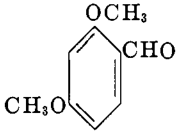
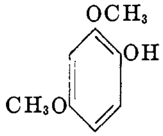
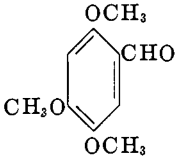
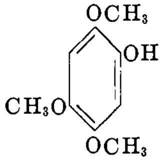
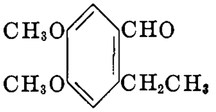
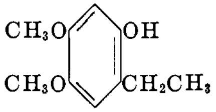
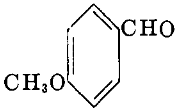
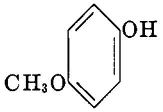
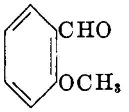
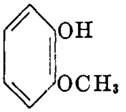
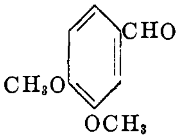
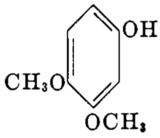
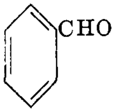
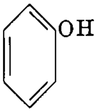
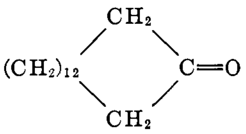
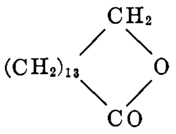
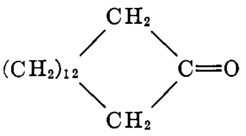
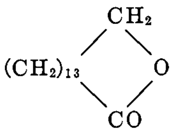
NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
1...		H_2O_2 in ether		(59)
2...		H_2O_2 in ether		(59)
3...		H_2O_2 in ether		(59)
4...		H_2O_2 in ether		(59)
5...		H_2O_2 in ether		(59)
6...		H_2O_2 in ether		(59)
7...		H_2O_2 in ether	 (only 0.7 per cent)	(59)
8...		H_2O_2, H_2SO_4		(66)
9...		$HOOSO_3H$, CH_3COOH		(56)

TABLE 7—*Continued*

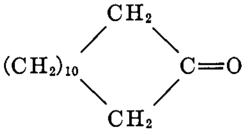
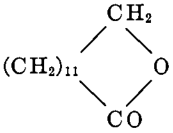
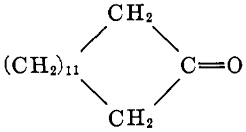
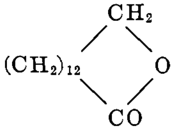
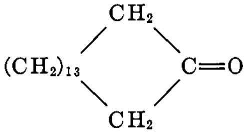
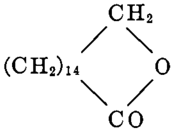
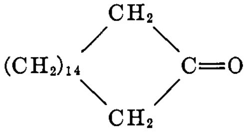
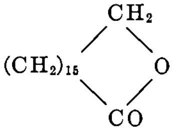
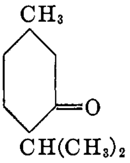
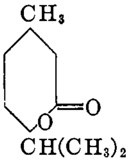
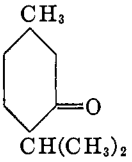
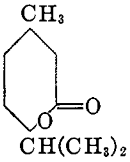
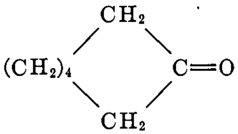
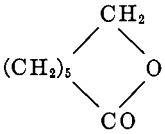
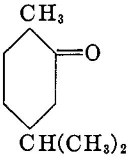
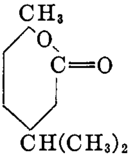
NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
10...		$HOOSO_3H$, CH_3COOH		(56)
11...		$HOOSO_3H$, CH_3COOH		(56)
12...		$HOOSO_3H$, CH_3COOH		(56)
13...		$HOOSO_3H$, CH_3COOH		(56)
14...	$C_6H_5COC_6H_5$	H_2O_2, H_2SO_4	$C_6H_5COOC_6H_5$	(21)
15...		H_2O_2, H_2SO_4		(21)
16...		$HOOSO_3H$		(3)
17...		$HOOSO_3H$		(3)
18...		$HOOSO_3H$		(2)

TABLE 7—*Continued*

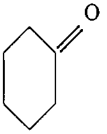
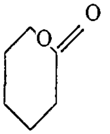
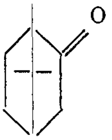
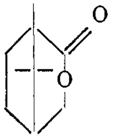
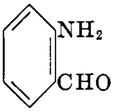
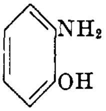
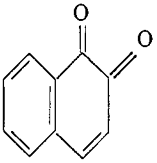
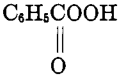
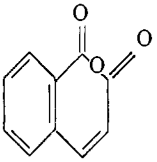
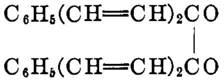
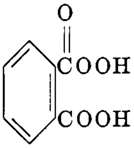
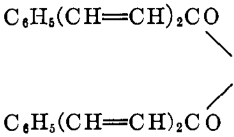
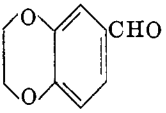
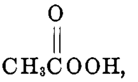
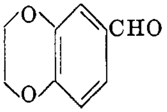
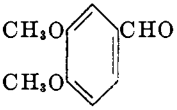
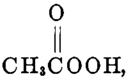
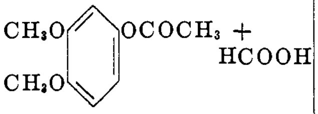
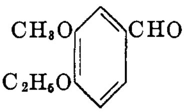
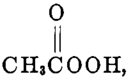
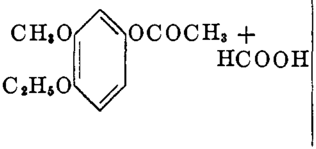
NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
19...		$HOOSO_3H$		(2)
20...		$HOOSO_3H$		(2)
21...		$HOOSO_3H$		(4)
22...		 $C_6H_5\underset{\underset{O}{\|}}{C}OOH$		(42)
23...	 $\begin{array}{l}C_6H_5(CH{=}CH)_2CO\\ \qquad\qquad\qquad\;\; \vert\\ C_6H_5(CH{=}CH)_2CO\end{array}$			(41)
24...		 $CH_3\overset{\overset{O}{\|}}{C}OOH,$ CH_3COOH, H^+	HCOOH + 	(7)
25...		 $CH_3\overset{\overset{O}{\|}}{C}OOH,$ trace of p-$CH_3C_6H_4SO_3H$		(8)
26...		 $CH_3\overset{\overset{O}{\|}}{C}OOH,$ trace of p-$CH_3C_6H_4SO_3H$		(8)

TABLE 7—*Continued*

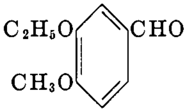
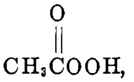
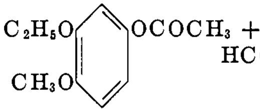
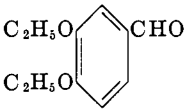
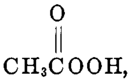
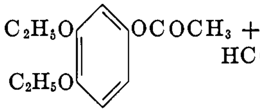
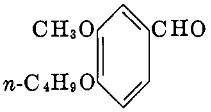
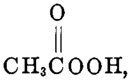
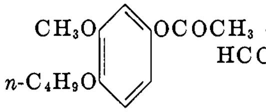
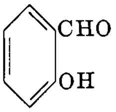
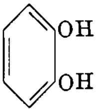
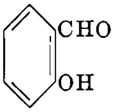
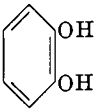
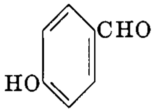
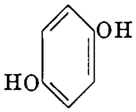
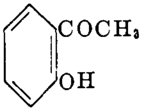
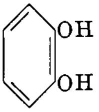
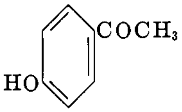
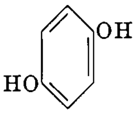
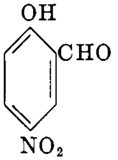
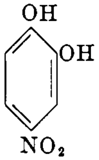
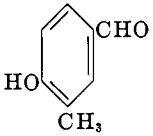
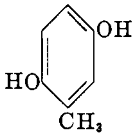
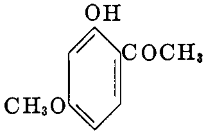
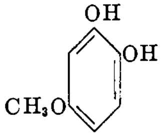
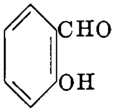
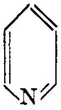
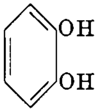
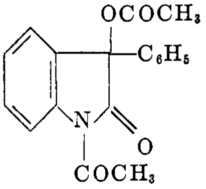
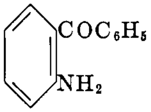
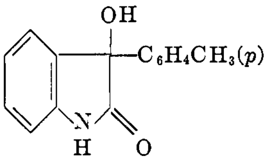
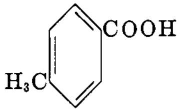
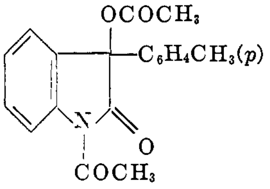
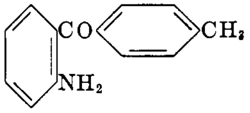
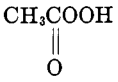
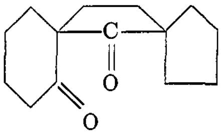
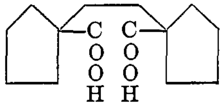
NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
27...		 $CH_3\overset{\overset{O}{\|}}{C}OOH$, trace of p-$CH_3C_6H_4SO_3H$	 $+$ HCOOH	(8)
28...		 $CH_3\overset{\overset{O}{\|}}{C}OOH$, trace of p-$CH_3C_6H_4SO_3H$	 $+$ HCOOH	(8)
29...		 $CH_3\overset{\overset{O}{\|}}{C}OOH$, trace of p-$CH_3C_6H_4SO_3H$	 $+$ HCOOH	(8)
30...		H_2O_2, CH_3COOH		(69)
31...	$(p\text{-}O_2NC_6H_4)_2CO$	H_2O_2, H_2SO_4	p-$O_2NC_6H_4COOH$ + p-$O_2NC_6H_4OH$	(23)
32...	p-$O_2NC_6H_4COC_6H_5$	H_2O_2, H_2SO_4	p-$O_2NC_6H_4COOH$ + C_6H_5OH	(23)
33...		H_2O_2, NH_3		(17)
34...		H_2O_2, NH_3		(17)
35...		H_2O_2, NH_3		(17)
36...		H_2O_2, NH_3		(17)

TABLE 7—*Concluded*

NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
37...		H_2O_2, NH_3		(17)
38...		H_2O_2, NH_3		(17)
39...		H_2O_2, NH_3		(17)
40...		H_2O_2, 		(68)
41...		H_2O_2, OH^-		(39)
42...		H_2O_2, OH^-		(39)
43...		H_2O_2, OH^-		(39)
44...	$C_6H_5CH{=}CHCOCH_3$	 $CH_3\underset{\underset{\displaystyle O}{\Vert}}{C}OOH$	$C_6H_5CH{=}CHOCOCH_3$	(9)
45...		H_2O_2, CH_3COOH		(45)

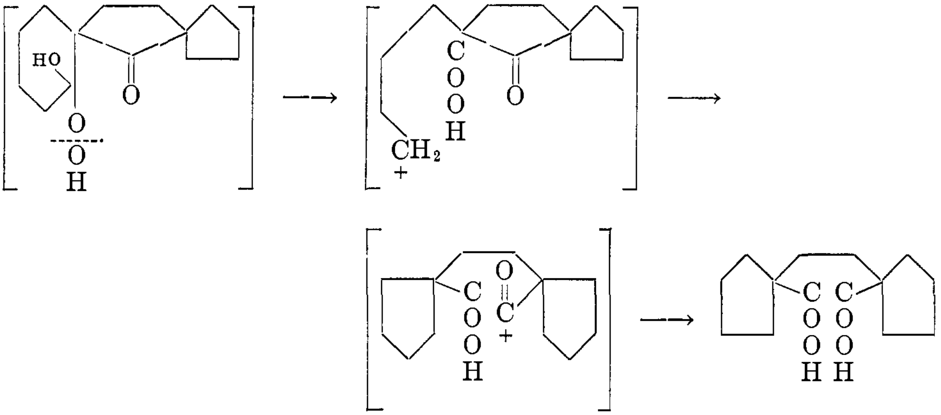
The various products can all be explained on the basis of the above scheme, except that the reactions of the α-diketones may involve cyclic intermediates.

Acetone reacts largely according to path (*a*), giving dimeric peroxide. Cyclic ketones, however, tend to react by path (*b*), giving lactones (3, 21, 56). Similarly, diketones give acid anhydrides (41, 42).

Support for the ionic mechanism is found in the observation of Dilthey *et al.* (21) that strong acid favors ester formation, while more dilute acid gives more of the dimeric peroxide. Acid apparently helps remove the sulfate ion in step (*b*).

The addition of hydroperoxides to carbonyl compounds can be catalyzed by either acid or base. In the former case a proton is added to the carbonyl oxygen; in the latter the attacking reagent is the anion of the hydroperoxide.

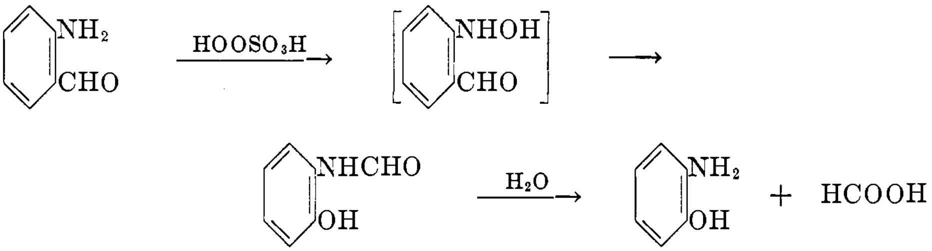
Reaction 45 of table 7, being more complicated than the others, deserves a little comment. It probably starts by addition of hydrogen peroxide and then involves a rearrangement accompanied by a displacement.



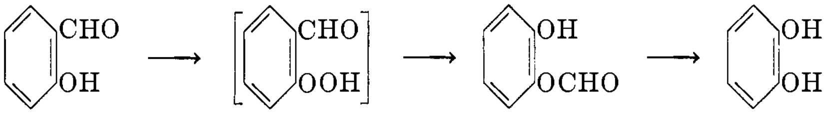
Aldehydes normally give carboxylic acids (scheme (*b*) of page 405; R′ equals H). But when the group attached to the carbonyl is of the type likely to migrate in a carbonium ion, a certain amount of phenol, quinone (1), or (in the case of aliphatic aldehydes) degradation product is obtained. The nature of the groups favoring phenol formation (Dakin reaction) is such as to support the ionic mechanism; thus, vanillin gives the phenol while acetylvanillin gives only the acid (8). Scheme (*b*) of page 405 of course predicts not the phenol but the corresponding formate. In some cases the intermediate formates have been isolated (67).

Oleic acid ozonide has also been used as a reagent for the conversion of suitably substituted benzaldehydes to the corresponding phenols (69). Rieche (55) has shown that a decomposing ozonide gives some α-hydroxyhydroperoxide and that the latter can give up hydrogen peroxide to other carbonyl compounds. The mechanism of the oxidation with decomposing oleic acid ozonide need not then be different from that with the more usual reagents.

The mechanism proposed on page 405 is not the only one that can be written for the Dakin reaction. In 1903 Bamberger oxidized *o*-aminobenzaldehyde with Caro's acid to *o*-aminophenol. He isolated from the reaction mixture the *N*-formyl derivative of *o*-aminophenol, which led him to postulate the following reaction mechanism (4):

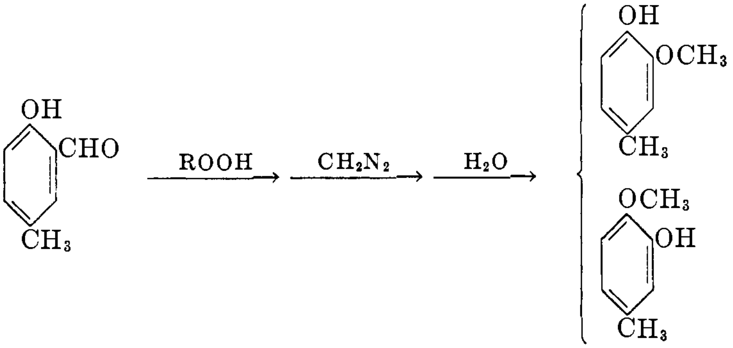


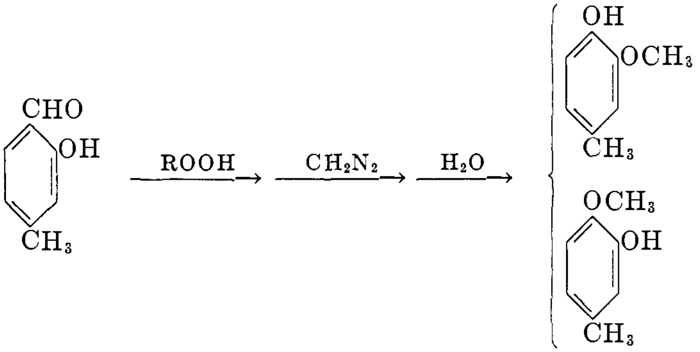
Wacek and Eppinger (68) proposed a similar mechanism for the Dakin reaction (alkaline hydrogen peroxide):



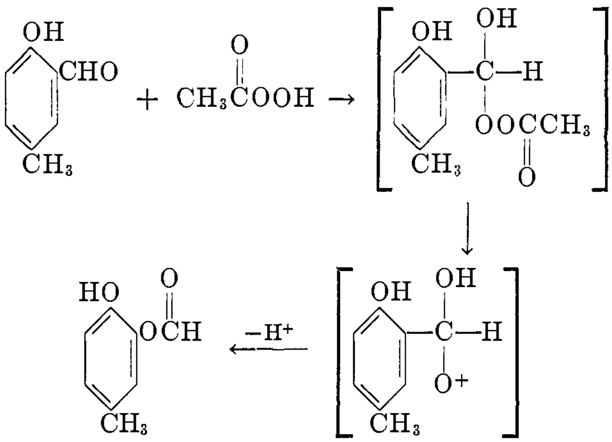
Their mechanism was supported by the fact that phenol is oxidized by hydrogen peroxide to hydroquinone and catechol.

But when Böeseken and his collaborators (8) showed that a free hydroxyl group was not necessary, it become obvious that a new mechanism was needed, at least for such cases. Wacek and Bézard (67) then developed reaction conditions which allowed the isolation of the intermediate catechol monoformate. They ran similar oxidations of methyl-substituted hydroxybenzaldehydes, hydrolyzing the reaction mixtures after treatment with diazomethane to methylate the unformylated hydroxyl. The product in each case was not just the substance predicted by their mechanism nor that predicted by the mechanism of page 405, but a mixture of both.





The mechanism which leads to the direct replacement of the formyl group by the formyloxy group is probably:

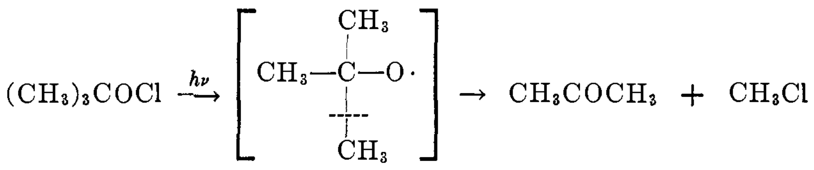


The other isomer is formed either by the mechanism of Wacek and Eppinger or by *trans*-esterification.

Aliphatic aldehydes are subject to the same sort of reaction. Acetaldehyde with hydrogen peroxide gives not only acetic acid but also some methane, probably from a methyl radical (6, 27). Propionaldehyde gives some acetic acid, formic acid, carbon dioxide, and ethane (6).

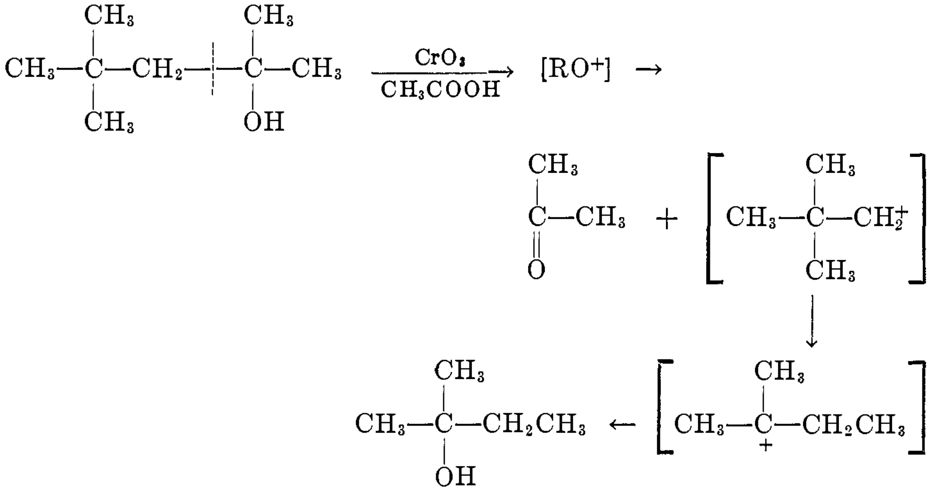
IV. OXIDATION OF ALCOHOLS

Decomposition of peroxides is not the only source of oxygen radicals and cations. Oxygen radicals are very probably produced, for example, in the photolysis of alkyl hypochlorites. Thus (11):



$$(CH_3)_3COCl \xrightarrow{h\nu} \left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot \right] \rightarrow CH_3COCH_3 + CH_3Cl$$

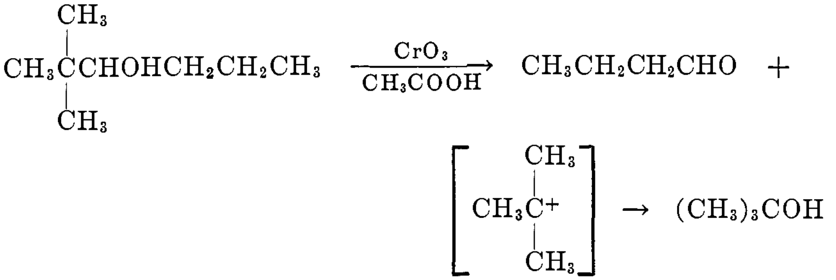
Mosher and his coworkers (47, 48) have found evidence of oxygen cations as intermediates in the chromic anhydride oxidation of alcohols:



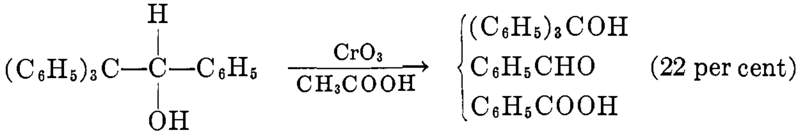
$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_3} \xrightarrow[\mathrm{CH_3COOH}]{\mathrm{CrO_3}} [\mathrm{RO^+}] \rightarrow \mathrm{\underset{O}{\overset{CH_3}{C}}{-}CH_3} + \left[\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2^+}\right]$$

$$\left[\mathrm{CH_3{-}C(CH_3)_2{-}CH_2^+}\right] \downarrow \left[\mathrm{CH_3{-}\underset{+}{\overset{CH_3}{C}}{-}CH_2CH_3}\right] \longrightarrow \mathrm{CH_3{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_2CH_3}$$

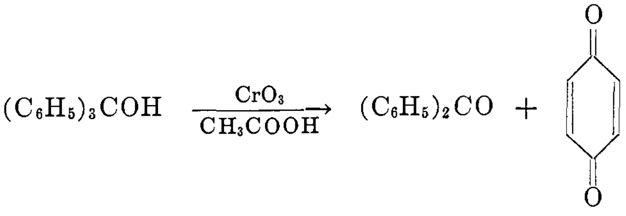
(10 per cent yield)



$$\mathrm{CH_3\underset{CH_3}{\overset{CH_3}{C}}CHOHCH_2CH_2CH_3} \xrightarrow[\mathrm{CH_3COOH}]{\mathrm{CrO_3}} \mathrm{CH_3CH_2CH_2CHO} + \left[\mathrm{CH_3\underset{CH_3}{\overset{CH_3}{C}}{}^+}\right] \rightarrow \mathrm{(CH_3)_3COH} \qquad (47)$$



$$\mathrm{(C_6H_5)_3C{-}\underset{OH}{\overset{H}{C}}{-}C_6H_5} \xrightarrow[\mathrm{CH_3COOH}]{\mathrm{CrO_3}} \begin{cases}\mathrm{(C_6H_5)_3COH} \\ \mathrm{C_6H_5CHO} \quad \text{(22 per cent)} \\ \mathrm{C_6H_5COOH}\end{cases} \qquad (48)$$



$$\mathrm{(C_6H_5)_3COH} \xrightarrow[\mathrm{CH_3COOH}]{\mathrm{CrO_3}} \mathrm{(C_6H_5)_2CO} + \qquad (48)$$

Fleury *et al.* (26) report the following reaction under conditions that leave acetone unscathed:

$$\mathrm{CH_3CHOHCH_2COOH} \xrightarrow[\mathrm{CrO_3}]{\mathrm{HNO_3}} \mathrm{CH_3COOH} + \mathrm{CO_2} + \mathrm{H_2O}$$

Since the reaction presumably does not involve acetoacetic acid and acetone, it is not unlikely that the first step is removal of a hydride ion from the alcohol, as in the reactions studied by Mosher.

There are a number of aromatic substitution reactions in which a carbinol group para to an amino group is replaced by a nitro group or bromine atom (14, 15, 24, 43). Such reactions go at very low temperatures. It is not at present possible to decide whether these reactions are true electrophilic substitutions, or examples of carbinol oxidation by the oxygen cation mechanism.

I wish to thank Professor Paul Doughty Bartlett for his many helpful suggestions.

V. REFERENCES

(1) ARNOLD, R. T., AND LARSON, R.: J. Org. Chem. **5**, 250 (1940).
(2) BAEYER, A., AND VILLIGER, V.: Ber. **32**, 3625 (1899).
(3) BAEYER, A., AND VILLIGER, V.: Ber. **33**, 858 (1900).
(4) BAMBERGER, E.: Ber. **36**, 2042 (1903).
(5) BARTLETT, P. D., AND LEFFLER, J. E.: Unpublished data.
(6) BEZZI, S.: Gazz. chim. ital. **63**, 345 (1933).
(7) BÖESEKEN, J., COHEN, W. D., AND KIP, C. J.: Rec. trav. chim. **55**, 815 (1936).
(8) BÖESEKEN, J., AND GREUP, J.: Rec. trav. chim. **58**, 528 (1939).
(9) BÖESEKEN, J., AND SOESMANN, A. L.: Rec. trav. chim. **52**, 874 (1933).
(10) BRETSCHNEIDER, H.: Ber. **74**, 1360 (1941).
(11) CHATTAWAY, F. D., AND BECKEBERG, O. G.: J. Chem. Soc. **123**, 2999 (1923).
(12) CHAVANNE, G., AND MILLER, O.: Bull. soc. chim. Belg. **40**, 611 (1931).
(13) CHAVANNE, G., PAHLAVOUNI, AND KATZENSTEIN: Bull. soc. chim. Belg. **40**, 626 (1931).
(14) CLARKE, L., AND ESSELEN, G. L.: J. Am. Chem. Soc. **33**, 1135 (1911).
(15) CLARKE, L., AND PATCH, R. H.: J. Am. Chem. Soc. **34**, 912 (1912).
(16) CRIEGEE, R.: Ber. **77**, 722 (1944).
(17) DAKIN, H. D.: Proc. Chem. Soc. **25**, 194 (1909).
(18) DILTHEY, W., AND DAHM, F.: J. prakt. Chem. **141**, 61 (1934).
(19) DILTHEY, W., HENKELS, S., AND LEONHARD, M.: J. prakt. Chem. **151**, 97 (1936).
(20) DILTHEY, W., AND HOSCHEN, W.: J. prakt. Chem. **138**, 42 (1933).
(21) DILTHEY, W., INCKEL, M., AND STEPHAN, H.: J. prakt. Chem. **154**, 219 (1940).
(22) DILTHEY, W., AND QUINT, F.: J. prakt. Chem. **131**, 1 (1931).
(23) DILTHEY, W., QUINT, F., AND DIERICHS, H.: J. prakt. Chem. **151**, 25 (1938).
(24) ESSELEN, G. L., AND CLARKE, L.: J. Am. Chem. Soc. **36**, 308 (1914).
(25) FARMER, E. H., AND SUNDRALINGAM, A.: J. Chem. Soc. **1942**, 121.
(26) FLEURY, P., COURTOIS, J., AND COUSIN, D.: Bull. soc. chim. biol. **26**, 381 (1944).
(27) FRY, H. S., AND PAYNE, J. H.: J. Am. Chem. Soc. **53**, 1980 (1931).
(28) FUSON, R. C., BYERS, D. J., AND RACHLIN, A. I.: J. Am. Chem. Soc. **64**, 2891 (1942).
(29) FUSON, R. C., BYERS, D. J., RACHLIN, A. I., AND SOUTHWICK, P. L.: J. Am. Chem. Soc. **64**, 2886 (1942).
(30) FUSON, R. C., LINDSEY, R. V., JR., AND WELLDON, P. B.: J. Am. Chem. Soc. **64**, 2888 (1942).
(31) FUSON, R. C., MAYNERT, E. W., AND SHENK, W. J., JR.: J. Am. Chem. Soc. **67**, 1939 (1945).
(32) GELISSEN, H., AND HERMANS, P. H.: Ber. **58**, 476 (1925).
(33) GEORGE, P., AND WALSH, A. D.: Trans. Faraday Soc. **42**, 94 (1946).
(34) HARRIS, E. J.: Proc. Roy. Soc. (London) **A173**, 126 (1939).
(35) HASSELSTRÖM, T.: Ann. Acad. Sci. Fennicae **A26**, No. 8, 3 (1927).

(36) Hasselström, T.: Ann. Acad. Sci. Fennicae **A29**, No. 5 (1927).
(37) Hey, D. H.: J. Chem. Soc. **1934**, 1966.
(38) Hock, H., and Gänicke, K.: Ber. **71**, 1430 (1938).
(39) Inagaki, S.: J. Pharm. Soc. Japan **59**, 7 (1939).
(40) Janot, M., and Chaigneau, M.: Compt. rend. **214**, 746 (1942).
(41) Karrer, P., Cochand, C., and Neuss, N.: Helv. Chim. Acta **29**, 1836 (1946).
(42) Karrer, P., and Schneider, L.: Helv. Chim. Acta **30**, 859 (1947).
(43) Kohler, E. P., and Patch, R. H.: J. Am. Chem. Soc. **38**, 1205 (1916).
(44) Kohler, E. P., and Thompson, R. S.: J. Am. Chem. Soc. **59**, 887 (1937).
(45) Mannich, C.: Ber. **74**, 1007 (1941).
(46) Milas, N. A., and Perry, L. H.: J. Am. Chem. Soc. **68**, 1938 (1946).
(47) Mosher, W. A., Langerak, E. O., and Coleman, J. J., Jr.: Abstracts of papers presented at the 112th Meeting of the American Chemical Society, New York City, September, 1947, p. 11L.
(48) Mosher, W. A., Neidig, H. A., and Huber, M. L.: Abstracts of papers presented at the 112th Meeting of the American Chemical Society, New York City, September 1947, p. 48L.
(49) Nauta, W. T., and Wuis, P. J.: Rec. trav. chim. **57**, 41 (1938).
(50) Overhoff, J., and Tilman, G.: Rec. trav. chim. **48**, 993 (1929).
(51) Pacquot, C.: Bull. soc. chim. France **8**, 695 (1941).
(52) Palmén, J.: Finska Keminstsamfundets Medd. **38**, 124 (1929).
(53) Pfeiffer, P., and Jaensch, E.: J. prakt. Chem. **159**, 241 (1941).
(54) Quint, F., and Dilthey, W.: Ber. **64**, 2082 (1931).
(55) Rieche, A.: *Alkylperoxide und Ozonide*. T. Steinkopff, Dresden and Leipzig (1931).
(56) Ruzicka, L., and Stoll, M.: Helv. Chim. Acta **11**, 1159 (1928).
(57) Späth, E., and Pailer, M.: Ber. **73**, 238 (1940).
(58) Späth, E., Pailer, M., and Gergely, G.: Ber. **73**, 795 (1940).
(59) Späth, E., Pailer, M., and Gergely, G.: Ber. **73**, 935 (1940).
(60) Staudinger, H.: Ber. **58**, 1075 (1925).
(61) Staudinger, H.: Ber. **58**, 1088 (1925).
(62) Staudinger, H., Dyckerhoff, K., Kleuer, H. W., and Ruzicka, L.: Ber. **58**, 1079 (1925).
(63) Stephens, H. N.: J. Am. Chem. Soc. **48**, 2920 (1926).
(64) Stephens, H. N.: J. Am. Chem. Soc. **50**, 187 (1928).
(65) Stephens, H. N., and Roduta, F. L.: J. Am. Chem. Soc. **57**, 2380 (1935).
(66) Stoll, M., and Scherrer, W.: Helv. Chim. Acta **13**, 142 (1930).
(67) Wacek, A., and Bézard, A.: Ber. **74**, 845 (1941).
(68) Wacek, A., and Eppinger, H. O.: Ber. **73**, 644 (1940).
(69) Wacek, A., Eppinger, H. O., and Bézard, A.: Ber. **73**, 521 (1940).
(70) Walsh, A. D.: Trans. Faraday Soc. **42**, 276 (1946).
(71) Wieland, H.: Ber. **44**, 2550 (1911).
(72) Wieland, H., and Maier, J.: Ber. **64**, 1205 (1931).
(73) Wieland, H., and Rasuwajew, G.: Ann. **480**, 157 (1930).
(74) Wieland, H., Schapiro, S., and Metzger, H.: Ann. **513**, 93 (1934).
(75) Young, W. G., McKinnis, A. C., Webb, I. D., and Roberts, J. D.: J. Am. Chem. Soc. **68**, 293 (1946).

APPENDIX[2]

Since this review was written, but before it went to press, there have appeared several very important papers on oxygen cations; there is also considerable research in progress.

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[2] Added August 29, 1949.

R. Criegee (Ann. **560,** 127 (1948)) has found that esters of decalin hydroperoxide decompose faster in media of higher dielectric constant. He therefore proposes that the reaction goes by way of an oxygen cation, which then rearranges with migration of a group from carbon to oxygen.

In the same paper Criegee proposes ionic mechanisms similar to those in this review for the ozonization of olefins and for the oxidation of ketones by Caro's acid. Waters (J. Chem. Soc. **1948,** 1574) has proposed ionic mechanisms for the oxidation of ketones with peracids in general. Strong confirmation for the Criegee–Waters mechanism is supplied by the kinetic study of S. L. Friess (J. Am. Chem. Soc. **71,** 2571 (1949)), who finds that the rate-determining step, in the case of perbenzoic acid, is the acid-catalyzed addition of the perbenzoic acid to the ketone. The rates of the oxidation reaction parallel the rates of semicarbazone formation for the same series of ketones.

H. H. Zeiss (J. Am. Chem. Soc. **70,** 858 (1948)) has proposed an oxygen cation intermediate for the chromic acid oxidation of tertiary alcohols. N. Kharasch, speaking at the Organic Symposium held at Madison, Wisconsin, in 1949, reported that cumene hydroperoxide decomposes either by an ionic mechanism to give acetone and phenol or by a radical mechanism to give acetophenone, depending on the reaction conditions. The present author (J. Am. Chem. Soc., to appear soon) has found that *p*-methoxy-*p'*-nitrobenzoyl peroxide may decompose by either the radical or the ionic mechanism. Ionic decomposition gives a *p*-methoxybenzoxy cation, which rearranges; the rearranged cation is isolated as the *p*-methoxyphenyl ester of *p*-nitrobenzoic carbonic anhydride.