SOME ORGANIC PEROXIDES AND THEIR REACTIONS

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IT has been known for a considerable time that certain classes of organic compound, especially ethers and olefins, peroxidise on storage and that such peroxides cause danger during distillation. This danger has generally been avoided by catalytic decomposition of the peroxide or by the addition of an antioxidant to the compound concerned so as to prevent the formation of peroxidic products.

During recent years peroxides have been isolated from a considerable number of compounds, and purified to varying degrees ; in some cases the chemical reactions of these peroxides have been studied. More extensive study of their reactions allied to a solution of the problem of their safe production and control on a large scale may well lead to their taking their place with other classes of compound as valuable industrial intermediates. Whether this proves true or not, there is no doubt that many oxidation reactions utilised in present-day processes proceed through a peroxide stage.

In this Review no mention is made of diacyl peroxides or of the catalytic effect of peroxides in telomerisation and reactions involving addition of halogen compounds and esters to olefins, so adequately studied by Kharasch. An attempt has been made to summarise the methods of formation and chemical reactions of certain classes of organic peroxide ; the production and interaction of radicals play a large part in peroxide chemistry. The only collected information previously available in this field has been due to A. Rieche,[1, 2] although a review of reactions of per-acids has recently appeared.[3] Two further reviews [4] have discussed peroxide formation and decomposition under a variety of conditions in the light of the possible mechanisms for such reactions.

1. Aliphatic Peroxides

(A) Alkyl Hydroperoxides (RO·OH).—Alkyl hydroperoxides have been produced by two main methods : (i) by reaction of hydrogen peroxide with alkyl sulphates (alcohol + sulphuric acid) in the presence of acid or alkaline catalysts, and (ii) by controlled oxidation of a hydrocarbon. The first method is of greater general application, since the required alcohol can often be made available whilst the corresponding hydrocarbon may not conveniently be oxidised to the hydroperoxide or only in very poor yield ; isolation may also be more difficult from the mixture of products given by the second

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[1] " Alkylperoxyde und Ozonide ", Steinkopff, 1931.

[2] " Die Bedeutung der Organischen Peroxyde für die chemische Wissenschaft u. Technik " ; Sammlung chemischer u. chem.-technischer Vorträge, 1936, **34.**

[3] D. Swern, *Chem. Reviews*, 1949, **45,** 1.

[4] J. E. Leffler, *ibid.*, p. 385 ; C. E. Frank, *ibid.*, 1950, **46,** 155.

method. However, hydroperoxide concentrates have been isolated from the oxidation of kerosene fractions in the presence of magnesium oxide,[5] and oxidised 2 : 7-dimethyloctane yields a 2-hydroperoxide and a 2 : 3-dihydroperoxide although one might have expected a 2 : 7-dihydroperoxide.[6]

Rather ill-defined peroxides in fairly low concentration have been reported by oxidation of pentane, hexane, and octane,[7] heptane and *iso*heptane,[8] and *n*-hexadecane,[9] whilst tertiary alkyl (especially *tert.*-butyl) hydroperoxides together with the ditertiary alkyl peroxides and other oxygenated products have been made by oxidation of branched-chain hydrocarbons in the presence of traces of hydrogen bromide as catalyst.[10]

Many hydroperoxides have been prepared by method (i) in a state of reasonable purity; they include the hydroperoxides of methyl,[1, 11] ethyl,[1, 12, 13, 14] propyl,[15] *iso*propyl,[14, 15] *sec.*-butyl,[14] *tert.*-butyl,[14, 16–19] *tert.*-amyl,[14, 20] triethylmethyl,[19] 1 : 1 : 2 : 2-tetramethylethyl,[19] pentamethylethyl,[19] ethylene glycol, and ethers of glycols,[14] whilst 2 : 5-dihydroperoxy-2 : 5-dimethylhexane and 2 : 7-dihydroperoxy-2 : 7-dimethyloctane have been similarly prepared.[19]

The lower members of the series are explosive and susceptible to shock, sharp surfaces, and warming, but as the C : O ratio increases these peroxides become less explosive although thermal decomposition is vigorous, with evolution of gas and steam.

Thermal decomposition brings about fission of the molecule, and the types of product given are dependent on the radicals formed. Methyl hydroperoxide gives rise to methanol, formaldehyde, formic acid, dimethyl ether, oxides of carbon, and water.[21] *tert.*-Butyl hydroperoxide (at 250°) yields acetone, methanol, *tert.*-butanol, and water,[18] although the proportion of decomposition products appears to vary with the temperature and at 100° the main product is *tert.*-butanol. The peroxides from C_{15} to C_{25} hydrocarbons yield ketones when heated.[22]

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[5] U.S.P. 2,447,794 (Union Oil Co.).

[6] K. I. Ivanov, V. K. Savinova, and V. P. Zhakhovskaya, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **59**, 703.

[7] P. Mondain-Monval and B. Quanquin, *Compt. rend.*, 1930, **191**, 299.

[8] K. I. Ivanov, *Acta Physicochim. U.S.S.R.*, 1938, **9**, 421.

[9] C. Kroger and A. Kaller, *Oel u. Kohle*, 1943, **39**, 669.

[10] U.S.P. 2,395,523, 2,403,758, 2,403,771, 2,403,772, 2,434,888, 2,446,797 (Shell Dev. Co.).

[11] A. Rieche and F. Hitz, *Ber.*, 1929, **62**, 2458.

[12] A. Baeyer and V. Villiger, *ibid.*, 1901, **34**, 738.

[13] A. Rieche and F. Hitz, *ibid.*, 1929, **62**, 2478.

[14] N. A. Milas, U.S.P. 2,176,407.

[15] S. S. Medvedev and E. Alekseeva, *Ber.*, 1932, **65**, 133; *J. Gen. Chem. Russia*, 1931, **1**, 1193, 1200.

[16] N. A. Milas, U.S.P. 2,223,807.

[17] N. A. Milas and S. A. Harris, *J. Amer. Chem. Soc.*, 1938, **60**, 2434.

[18] N. A. Milas and D. M. Surgenor, *ibid.*, 1946, **68**, 205.

[19] R. Criegee and H. Dietrich, *Annalen*, 1948, **560**, 135.

[20] N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 643.

[21] S. S. Medvedev and A. Podyapolskaya, *Acta Physicochim. U.S.S.R.*, 1935, **2**, 487.

[22] P. George, E. K. Rideal, and A. Robertson, *Nature*, 1942, **149**, 601.

Catalytic reduction leads to the formation of the corresponding alcohol by loss of one atom of oxygen.

Sodium sulphite is in general a much slower reducing agent, whilst the effect of ferrous sulphate is probably partly that of a reducing agent and partly catalytic.

This class of peroxide is relatively stable under mild acid conditions, whilst cold dilute alkali gives rise to the alkali-metal salt of the hydroperoxide. In the presence of concentrated or hot alkali, however, these hydroperoxides are unstable and decompose to aldehydes, ketones, and acids.[15]

Reaction with a further molecule of an alcohol in the presence of sulphuric acid is the normal route to the synthesis of a dialkyl peroxide:[23]

$$\mathrm{RO{\cdot}OH + R'OH \longrightarrow RO{\cdot}OR' + H_2O}$$

Thus *tert.*-butyl hydroperoxide undergoes a smooth reaction at $< 10°$ with ethyl sulphate and potassium hydroxide to yield ethyl *tert.*-butyl peroxide.[24] Alternatively the metal salt of the hydroperoxide may be made to react with an alkyl halide in an inert solvent in which the metal halide formed is insoluble.[25]

Organic acid chlorides react with alkyl hydroperoxides in a basic solvent (*e.g.*, pyridine) to yield per-esters; under mild hydrolytic conditions the hydroperoxide and acid can be regenerated. Many esters of *tert.*-butyl hydroperoxide have been prepared in this manner,[20] and the crystalline *p*-nitrobenzoates have recently been used by R. Criegee and H. Dietrich[26] for characterising several hydroperoxides; these authors state that esterification of *tert.*-alkyl hydroperoxides proceeds much more easily than with tertiary alcohols. These per-esters liberate iodine from acidic potassium iodide much more slowly than do the original hydroperoxides.

Aldehydes on reaction with hydroperoxides readily provide monohydroxydialkyl peroxides, $\mathrm{R'CH(OH){\cdot}O{\cdot}OR}$. Mineral-acid catalysts are generally used except in the case of formaldehyde, which is sufficiently reactive without the presence of a catalyst; the reaction may simply be carried out in ether[27] or water:[28]

$$\mathrm{RO{\cdot}OH + R'CHO \longrightarrow R'CH(OH){\cdot}O{\cdot}OR}$$

Ketones react in a similar fashion, but the product may, with an additional molecule of hydroperoxide, yield a diperoxy-compound:[29]

$$\mathrm{RO{\cdot}OH + R'COR'' \longrightarrow RO{\cdot}O{\cdot}CR'R''{\cdot}OH \xrightarrow{+RO{\cdot}OH} CR'R''(O{\cdot}OR)_2}$$

This reaction has been extended to keto-acids; for instance, lævulic acid gives $\mathrm{CH_3{\cdot}C(OH)(O{\cdot}OR){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$, although one might have expected lactonisation to follow yielding the γ-lactone.

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[23] (*a*) A. Rieche, *Ber.*, 1929, **62**, 218; (*b*) W. Bockmüller and L. Pfeuffer, *Annalen*, 1939, **537**, 178; (*c*) N. A. Milas and L. H. Perry, *J. Amer. Chem. Soc.*, 1946, **68**, 1938.

[24] U.S.P. 2,403,758, 2,414,769 (Shell Dev. Co.).

[25] U.S.P. 2,403,709 (Shell Dev. Co.).

[26] *Annalen*, 1948, **560**, 135.

[27] A. Rieche, *Ber.*, 1930, **63**, 2642.

[28] U.S.P. 2,400,041 (Shell Dev. Co.).

[29] U.S.P. 2,455,569 (Shell Dev. Co.); F. H. Dickey *et al.*, *Ind. Eng. Chem.*, 1949, **41**, 1673; Q.T. Wiles *et al.*, *ibid.*, p. 1679.

Mention has recently been made in the patent literature of the addition of *tert.*-butyl hydroperoxide to activated double bonds,[30] *e.g.*, acrylonitrile or methyl acrylate :

$$\mathrm{CH_2{:}CH{\cdot}CN + CMe_3{\cdot}O{\cdot}OH \longrightarrow CMe_3{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN}$$
$$\mathrm{CH_2{:}CH{\cdot}CO_2Me + CMe_3{\cdot}O{\cdot}OH \longrightarrow CMe_3{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me}$$

(B) Hydroxyalkyl Hydroperoxides [$\mathrm{RCH(OH){\cdot}O{\cdot}OH}$].—These compounds have been prepared by reaction of hydrogen peroxide with aliphatic aldehydes, preferably in an anhydrous medium (*e.g.*, ether). In aqueous solution the tendency is to the formation of bishydroxyalkyl peroxides, $\mathrm{RCH(OH){\cdot}O{\cdot}O{\cdot}CHR{\cdot}OH}$; hydroxymethyl hydroperoxide could only be prepared from anhydrous formaldehyde.[31]

The C_7 to C_{12} homologues are solids with melting points ranging from 40° to 67°.[32] Ketomalonic ester on treatment with hydrogen peroxide in ether similarly gives a mixture of hydroxydicarbethoxymethyl hydroperoxide, $\mathrm{C(OH)(CO_2Et)_2O{\cdot}OH}$ and di(hydroxydicarbethoxymethyl) peroxide, $\mathrm{[C(OH)(CO_2Et)_2O{\cdot}]_2}$.[33]

The alkyl hydroxy-hydroperoxides are insoluble in water, but are slowly decomposed by it to give bishydroxyalkyl peroxides :

$$\mathrm{RCHO + H_2O_2 \longrightarrow RCH(OH){\cdot}O{\cdot}OH \xrightarrow[+\ water]{+\ RCHO} RCH(OH){\cdot}O{\cdot}O{\cdot}CHR{\cdot}OH}$$

Hydroxymethyl hydroperoxide explodes violently when heated in a flame, but the higher homologues on fusion or heating in acetic acid are converted into the acid corresponding to the aldehyde used in their preparation. Späth, Pailer, and Schmid [32b] had hoped to obtain the alcohol with one carbon atom less than the hydroxy-hydroperoxide by thermal treatment, but found that the acid was the main product in every case.

Alkali also leads to formation of the corresponding acid :

$$\mathrm{RCH(OH){\cdot}O{\cdot}OH \xrightarrow{NaOH} RCO_2Na + H_2O}$$

Reaction of a hydroxy-hydroperoxide, $\mathrm{RCH(OH){\cdot}O{\cdot}OH}$, with an aldehyde, $\mathrm{R'CHO}$, leads to the unexpected result that the unsymmetrical bishydroxyalkyl peroxide, $\mathrm{RCH(OH){\cdot}O{\cdot}O{\cdot}CHR'{\cdot}OH}$, is not formed ; rearrangement leads to the production of two symmetrical compounds : [32a]

$$\mathrm{2RCH(OH){\cdot}O{\cdot}OH + 2R'CHO \longrightarrow RCH(OH){\cdot}O{\cdot}O{\cdot}CHR{\cdot}OH + R'CH(OH){\cdot}O{\cdot}O{\cdot}CHR'{\cdot}OH}$$

The lower homologues are converted into mixtures of aldehydes and acids by ferrous sulphate.[31, 32a]

An interesting reaction involves dehydration of lower hydroxy-hydroperoxides with phosphoric oxide; very explosive, polymeric alkylidene peroxides are given ; the higher homologues under similar conditions provide acids.[32a]

(C) Dialkyl Peroxides ($\mathrm{RO{\cdot}OR'}$).—The lower members of this series

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[30] B.P. Appln. 16,783/48 (N.V. de Bataafsche P.M.).

[31] A. Rieche and R. Meister, *Ber.*, 1935, **68**, 1465.

[32] (*a*) A. Rieche, *ibid.*, 1931, **64**, 2328 ; (*b*) E. Spath, M. Pailer, and M. Schmid, *ibid.*, 1941, **74**, 1552.

[33] N. A. Milas and P. C. Panagiotakos, *J. Amer. Chem. Soc.*, 1946, **68**, 533.

have been known for over twenty years, and were prepared by treatment of hydrogen peroxide (or a hydroperoxide) with an alkyl sulphate in the presence of alkali.[34] Dimethyl peroxide is a gas at room temperature (b.p. 13·5°) and is so explosive that only about 2 g. can safely be prepared at a time.

The higher homologues have been prepared in the laboratory by the above method, with or without alkali, and by the reaction of alkyl halides with metal salts of hydroperoxides as mentioned previously : [25]

$$\mathrm{RO{\cdot}OM + R'X \longrightarrow RO{\cdot}OR' + MX}$$

Experiments carried out by the Shell Development Company have shown that branched-chain hydrocarbons (*e.g.*, *iso*butane and *iso*butene) when oxidised in the presence of hydrogen bromide yield *tert.*-alkyl peroxides and hydroperoxides amongst the products.[10] The peroxides have been separated from the hydroperoxides by azeotropic distillation with water.[35]

The lowest members are unstable and explosive and liberate little iodine from acidified potassium iodide solution.

Passage of the dialkyl peroxide through a heated tube causes formation of radicals, *e.g.*,

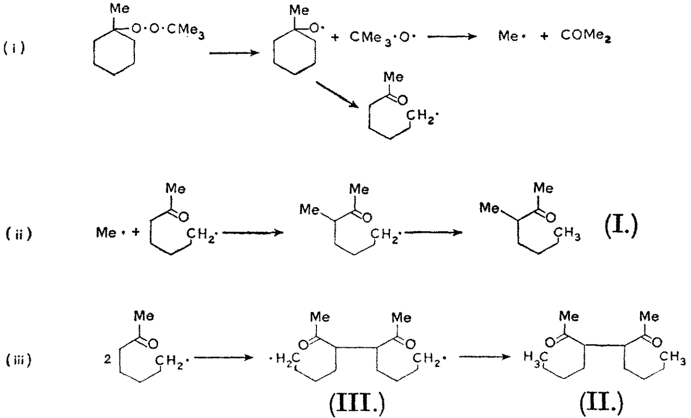
$$\mathrm{CMe_3{\cdot}O{\cdot}O{\cdot}CMe_3 \longrightarrow 2CMe_3{\cdot}O{\cdot} \longrightarrow Me{\cdot} + COMe_2}$$

$$\mathrm{Me{\cdot} + CMe_3{\cdot}O{\cdot}O{\cdot}CMe_3 \longrightarrow C_2H_6 + COMe_2 + CMe_3{\cdot}O{\cdot}}$$

The alkyl radicals may then undergo one of three reactions :

(*a*) They may dimerise to yield paraffins ; *e.g.*, di-*tert.*-butyl peroxide yields ethane (and acetone), whilst di-*tert.*-amyl peroxide provides butane (and acetone) ; [18, 20] similarly, di-(3-ethylpent-3-yl) peroxide gives mainly butane and diethyl ketone on heating, and *tert.*-butyl 1 : 1 : 2 : 2-tetramethyl-*n*-propyl peroxide yields *neo*pentane and acetone under comparable conditions.[23c]

(*b*) They may react with a different radical formed in the same decomposition ; *e.g.*, methyl*cyclo*hexyl *tert.*-butyl peroxide provides ethane, acetone, 3-methylheptan-2-one (I) and 3 : 4-dibutylhexane-2 : 5-dione (II), the suggested mechanism being : [23c]



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[34] A. Rieche and W. Brumshagen, *Ber.*, 1928, **61**, 951 ; A. Baeyer and V. Villiger, *ibid.*, 1900, **33**, 3387 ; A. Rieche and F. Hitz, *ibid.*, 1929, **62**, 218.

[35] U.S.P. 2,383,919 (Shell Dev. & Co.).

It does not appear obvious, however, why the diketone (II) should be formed in preference to tetradecane-2 : 13-dione by end-to-end addition of the radicals (III).

(*c*) They may further react with other compounds introduced simultaneously, *e.g.*, paraffins or olefins, for instance :

$$\mathrm{CHMe{:}CH_2 + Me\cdot \longrightarrow \cdot CHMe\cdot CH_2Me}, \text{ followed by}$$

(i) $\mathrm{\cdot CHMe\cdot CH_2Me + CMe_3\cdot O\cdot O\cdot CMe_3 \longrightarrow CHMe_2\cdot CH_2Me + 2COMe_2 + Me\cdot}$

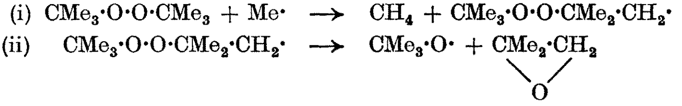
or

(ii) $\mathrm{CHMe{:}CH_2 + \cdot CHMe\cdot CH_2Me \longrightarrow \cdot CHMe\cdot CH_2\cdot CHMe\cdot CH_2Me}$

Thus, propene gives but-1-ene, but-2-ene, pentanes, and pentenes, whilst *iso*butene forms *neo*hexane, *iso*pentane, and tertiary pentenes ; allyl chloride yields 2-chlorobut-1-ene, 1-chlorobut-2-ene, and chloropentanes. The paraffins propane and *iso*butane lead to formation of *iso*butene and *neo*pentane.[36]

Reaction of peroxides with benzaldehyde similarly leads to formation of the radical PhCO·O·CHPh· which dimerises to *s*-diphenylethylene dibenzoate.[37]

It has been found that di-*tert.*-butyl peroxide decomposes in various solvents (cumene and *tert.*-butylbenzene) in a similar fashion to the thermal decomposition to give a mixture of *tert.*-butanol and acetone, but in a tertiary amine (tributylamine) the product consists almost entirely of the alcohol.[38] In the above reactions the alkyl (*e.g.*, methyl) radical when liberated has been able to react with another compound or radical present by addition, substitution, or removal of a hydrogen atom. In the liquid phase, thermal decomposition of di-*tert.*-butyl peroxide, where no other compound is present, the methyl radical liberated abstracts hydrogen from a further molecule of the peroxide to leave a new radical which provides *iso*butene epoxide on decomposition : [39]



(i) $\mathrm{CMe_3\cdot O\cdot O\cdot CMe_3 + Me\cdot \longrightarrow CH_4 + CMe_3\cdot O\cdot O\cdot CMe_2\cdot CH_2\cdot}$

(ii) $\mathrm{CMe_3\cdot O\cdot O\cdot CMe_2\cdot CH_2\cdot \longrightarrow CMe_3\cdot O\cdot + CMe_2\cdot CH_2}$ (with O bridging $\mathrm{CMe_2}$ and $\mathrm{CH_2}$)

Under these conditions of decomposition the reaction products contain more epoxide than acetone or *tert.*-butanol.

Reduction of dialkyl peroxides, where possible, gives rise to the corresponding alcohols. Zinc and acid have been used for diethyl peroxide, and Raney nickel under pressure for di-*tert.*-butyl peroxide.

Treatment of dialkyl peroxides with a mixture of sulphur dioxide and chlorine (or bromine) at 0—20° in ultra-violet light leads to production of a sulphonyl halide.[41] Di-*tert.*-butyl peroxide on reaction at 0° with hydrogen bromide yields up to 64% of 1 : 2-dibromo-2-methylpropane.[40]

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[36] U.S.P. 2,396,206, 2,396,217 (Shell Dev. Co.) ; F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 95. [37] *Idem, ibid.*, p. 3258.

[38] J. H. Raley, F. F. Rust, and W. E. Vaughan, *ibid.*, p. 1336.

[39] E. R. Bell, F. F. Rust, and W. E. Vaughan, *ibid.*, 1950, **72**, 337.

[40] N. A. Milas and C. N. Winnick, *ibid.*, 1949, **71**, 748.

[41] B.P. Appln. 31,755/48 (N.V. de Bataafsche P.M.).

(D) Monohydroxydialkyl Peroxides [RCH(OH)·O·OR′].—This class of compound is usually prepared by reaction of hydroperoxides with aldehydes or ketones; ether or an excess of the carbonyl component may be used as solvent:

$$\mathrm{RO{\cdot}OH + R'COR'' \longrightarrow RO{\cdot}O{\cdot}CR'R''{\cdot}OH}$$

In general an acidic catalyst has been used,[27, 28, 29, 42] although formaldehyde readily reacts in the absence of catalyst, and in this respect there is a similarity with the reaction of the corresponding carbonyl compounds with hydrogen peroxide to yield hydroxy-hydroperoxides. An excess of the hydroperoxide in this reaction leads to formation of diperoxy-compounds as mentioned on p. 253.

Hydroxy-dialkyl peroxides are distillable liquids, rather less explosive than dialkyl peroxides and more stable than non-peroxidic semiacetals. Acid iodide only leads to liberation of *ca.* 50% of the iodine to be expected from the active oxygen.[1]

Little information is available concerning the products of thermal decomposition of these compounds, except that it has been stated that formaldehyde and other carbonyl compounds are formed.

An unexpected reaction is that, with alkali, it is claimed that atomic hydrogen is produced.[27, 28] Methyl hydroxymethyl peroxide also yields formic acid and methanol, whilst hydroxymethyl *tert.*-alkyl peroxides provide methane and hydrogen.

With ferrous sulphate an exothermic catalytic reaction takes place to yield an acid and an alcohol:

$$\mathrm{EtO{\cdot}O{\cdot}CH_2{\cdot}OH \longrightarrow EtOH + HCO_2H}$$

(E) Bishydroxyalkyl Peroxides [RCH(OH)·O·O·CHR·OH].—Like the hydroxyalkyl hydroperoxides these compounds are produced by reaction of hydrogen peroxide with aldehydes or ketones; a second molecule of carbonyl compound may also be added to a hydroxyalkyl hydroperoxide:

$$\mathrm{H_2O_2 + RCHO \rightleftharpoons RCH(OH){\cdot}O{\cdot}OH + RCHO \rightleftharpoons RCH(OH){\cdot}O{\cdot}O{\cdot}CHR{\cdot}OH}$$

Since these peroxides are more stable than the corresponding hydroperoxides, the above reactions tend to go to completion to the right in the presence of water.

Bishydroxymethyl peroxide has been produced, apart from by the normal route, by the decomposition of ethylene ozonide[43] and from the action of ozone on dimethyl ether.[44] The higher homologues, up to bishydroxydodecyl peroxide,[1] and halogenated peroxides, *e.g.*, from chloral,[45] have been prepared.

The first member of the series, $\mathrm{CH_2(OH){\cdot}O{\cdot}O{\cdot}CH_2(OH)}$, is a solid, m.p. 62—64°, but the next higher homologues are liquids. Bishydroxyheptyl peroxide (m.p. 69°) and further members are solids—bishydroxydodecyl peroxide has m.p. 84°.[1] They are non-explosive compounds—except the

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[42] B.P. 444,544 (N.V. de Bataafsche P.M.).

[43] E. Briner and P. Schnorf, *Helv. Chim. Acta*, 1929, **12**, 154.

[44] F. G. Fischer, *Annalen*, 1929, **476**, 244.

[45] A. Baeyer and V. Villiger, *Ber.*, 1900, **33**, 2481.

lowest member—and liberate iodine quantitatively from acid iodide solution.

Thermal decomposition of this series of compound leads to formation of a mixture of acid and aldehyde :

$$RCH(OH)\cdot O\cdot O\cdot CHR\cdot OH \longrightarrow RCHO + RCO_2H + H_2O$$

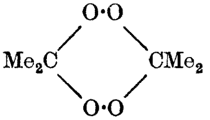
Warming with water leads to reconversion into aldehydes and hydrogen peroxide ; the aldehydes may often be removed from the reaction mixture in steam. Warm, dilute acid leads to a similar but faster reaction, and warm alkali also provides aldehyde and hydrogen peroxide except with the two lowest members of the series which yield the acid in addition.[1, 46]

As with the hydroxyalkyl hydroperoxides, it has been found that phosphoric oxide causes dehydration and production of the highly explosive alkylidene peroxides (see below), related in structure to ozonides. Thus bishydroxyethyl peroxide actually gives a mixture of the monomeric and dimeric ozonides of but-2-ene,[46b, 47] as proved by their decomposition with acid and alkali.[47] Several of these alkylidene peroxides have been isolated from different members of the series, and all appear to be very dangerous compounds, sensitive to shock.

Bishydroxymethyl peroxide forms derivatives with ammonia and other nitrogen compounds (urea and hydrazine) ;[1] however, di-(1-hydroxy-8-carboxyoctyl) peroxide on treatment with semicarbazide in ethanol yields the semicarbazone of the aldehydo-acid.[46a]

(F) Alkylidene Peroxides and Ether Peroxides.—The formation of ethylidene peroxide, $(\cdot CHMe\cdot O\cdot O\cdot)_x$, from hydroxyethyl hydroperoxide by treatment with phosphoric oxide has already been mentioned (p. 254), and this reaction can be extended to the corresponding propyl derivative. Ethylidene peroxide has also been found in the products of auto-oxidation of ether, and has been formed by heating butene ozonide *in vacuo.*[48]

These compounds are exceedingly explosive and sensitive to friction, and are decomposed by acid and alkali to the corresponding aldehyde and acid, respectively.



Dimeric acetone peroxide has been produced by reaction of solid Caro's reagents with acetone in ether[49] and from the ozonides of compounds with a terminal *iso*propylidene group (*e.g.*, mesityl oxide, citral, and squalene).[1] The inset structure has been suggested for this compound ; it has m.p. 132° and on catalytic decomposition affords acetic acid. Reduction with zinc and alkali leads to acetone.

Acetone also forms a trimeric peroxide by the action of hydrogen peroxide and mineral acid. It has m.p. 98°, and reacts with acids to regenerate acetone and hydrogen peroxide.

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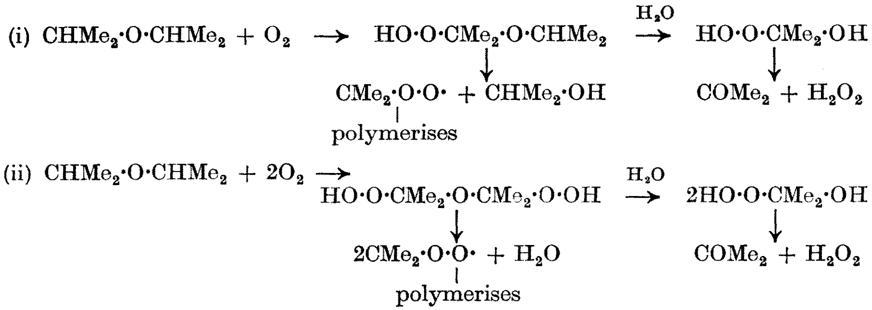
[46] (*a*) G. King, *J.*, 1942, 218 ; (*b*) A. Rieche, R. Meister, H. Sauthoff, and H. Pfeiffer, *Annalen*, 1942, **553,** 187.

[47] A. Rieche and R. Meister, *Ber.*, 1932, **65,** 1274.

[48] *Idem, ibid.*, 1931, **64,** 2335 ; 1939, **72,** 1933.

[49] A. Baeyer and V. Villiger, *ibid.*, 1899, **32,** 3628, 3632 ; 1900, **33,** 124.

A mixture of both peroxides is produced during the autoxidation of di*iso*propyl ether. One mechanism suggested [50] for such formation is :



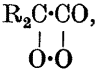
$$\begin{tikzcd}
\text{(i) } \mathrm{CHMe_2{\cdot}O{\cdot}CHMe_2 + O_2} \arrow[r] & \mathrm{HO{\cdot}O{\cdot}CMe_2{\cdot}O{\cdot}CHMe_2} \arrow[r, "\mathrm{H_2O}"] \arrow[d] & \mathrm{HO{\cdot}O{\cdot}CMe_2{\cdot}OH} \arrow[d] \\
& \mathrm{CMe_2{\cdot}O{\cdot}O{\cdot} + CHMe_2{\cdot}OH} \arrow[d, no head] & \mathrm{COMe_2 + H_2O_2} \\
& \text{polymerises} &
\end{tikzcd}$$

$$\begin{tikzcd}
\text{(ii) } \mathrm{CHMe_2{\cdot}O{\cdot}CHMe_2 + 2O_2} \arrow[r] & \mathrm{HO{\cdot}O{\cdot}CMe_2{\cdot}O{\cdot}CMe_2{\cdot}O{\cdot}OH} \arrow[r, "\mathrm{H_2O}"] \arrow[d] & \mathrm{2HO{\cdot}O{\cdot}CMe_2{\cdot}OH} \arrow[d] \\
& \mathrm{2CMe_2{\cdot}O{\cdot}O{\cdot} + H_2O} \arrow[d, no head] & \mathrm{COMe_2 + H_2O_2} \\
& \text{polymerises} &
\end{tikzcd}$$

Higher ketones also yield polymeric peroxides on treatment with hydrogen peroxide and sulphuric acid [51] or with Caro's acid.

It has also been claimed that peroxides are formed from lævulic acid and mesityl oxide,[1] although little has been done to study these compounds in detail.

(G) Alkenyl Peroxides.—(1) *Mono-olefins.*—The fact that olefins form peroxides in the presence of air has been known for a considerable time ; peroxides from pentene, trimethylethylene, and hexene have been reported,[52] and a polymeric keten peroxide, $\mathrm{R_2\underset{|}{C}{\cdot}\underset{|}{C}O}$ $\mathrm{O{\cdot}O}$, which decomposed to the ketone COR_2 and carbon dioxide, has also been described.[53]



$$\begin{array}{c}\mathrm{R_2C{\cdot}CO}\\ \mathrm{|\ \ |}\\ \mathrm{O{\cdot}O}\end{array}$$

A straight-chain olefin, *e.g.*, hex-1-ene, has been found to give a conversion into hydroperoxide of only 1·5—2%, even in the presence of a catalyst (*e.g.*, copper chloride), but mixed hexenes from dehydrated 2-methylpentan-1-ol gave up to 10% of hydroperoxide.[54] This seems to indicate that branching of the chain leads to greater ease of peroxide formation or greater stability of the peroxide compared with the corresponding straight-chain compound.

Peroxides from the lower olefins (propene, but-1- and -2-ene, *iso*butene, pent-1- and -2-ene, 2-methylbut-2-ene, hex-2-ene, and hept-3-ene) have been stated to be obtained [55] in 5% yield (+ 10% of other oxygenated products) by liquid-phase oxidation at − 50° to 150°.

It was suggested by J. L. Bolland [56] that the first stage in the oxidation of all olefins is the formation of a hydroperoxide at the α-methylene group, and only in the case of a diene is a cyclic peroxide considered to be possible.[56b] The work of E. H. Farmer and H. P. Koch also leads to such a viewpoint.

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[50] A. Rieche and K. Koch, *Ber.*, 1942, **75**, 1016 ; K. I. Ivanov, V. K. Savinova, and E. G. Mikhailova, *J. Gen. Chem. Russia*, 1946, **16**, 65, 1003, 1015.

[51] W. Dilthey, M. Inckel, and H. Stephan, *J. pr. Chem.*, 1940, **154**, 219.

[52] C. Engler, *Ber.*, 1900, **33**, 1094.

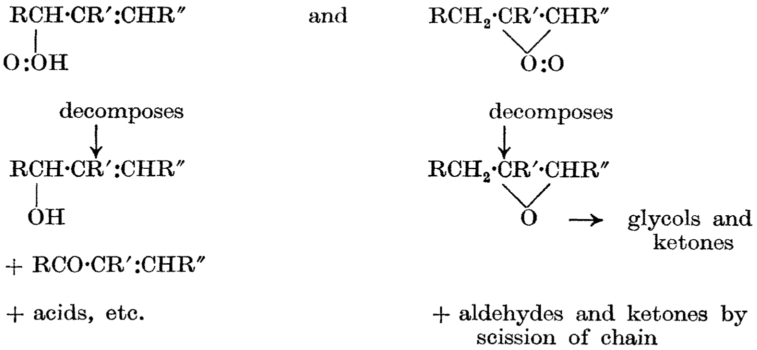
[53] J. d'Ans and W. Frey, *ibid.*, 1912, **45**, 1848.

[54] H. Hock and A. Neuwirth, *ibid.*, 1939, **72**, 1562.

[55] B.P. 614,456 (Petrocarbon).

[56] (*a*) *Quart. Reviews*, 1949, **3**, 1 ; (*b*) Bolland and H. Hughes, *J.*, 1949, 492.

However, C. Paquot [57] has suggested that two types of peroxide are formed by oxidation of olefins, *i.e.*, hydroperoxides and cyclic peroxides; these would both be expected to provide the different classes of decomposition products actually found. For instance, the olefin $CH_2R{\cdot}CR'{:}CHR''$ would give

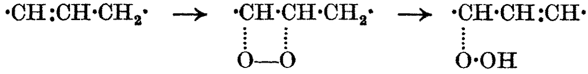


A similar type of cyclic peroxide has been suggested to explain the oxidation products of anethole (see p. 268).

Recently a preliminary study of the oxidation of various phenyl-substituted olefins has been carried out,[58] and, by restricting the uptake of oxygen to ½ mole per mole of olefin, in one case a product containing up to 65% of peroxide was obtained. At the same time the unsaturation decreased by about 43%, suggesting that cyclic or polymeric peroxides were formed: epoxide formation might well have partly accounted for this. Further oxidation led to a breakdown of the molecule to acids, carbon dioxide, and water.

Presumably such cyclic peroxides would be very unstable and may not be isolable from a simple olefin even if it should exist. However, whatever the mechanism of epoxide formation might be, the presence of such compounds amongst olefin oxidation products has been shown by Paquot; [59] a patent for the production of epoxides by oxidation of olefins in the presence of basic substances has been granted.[60]

In a similar way with the peroxides from unsaturated fatty acids and esters, a hydroperoxide has been isolated from methyl oleate [61] and methyl elaidate,[62] but it has been suggested [63] that a type of ring peroxide may be formed as an intermediate:



$$\cdot CH{:}CH{\cdot}CH_2\cdot \longrightarrow \cdot CH{\cdot}CH{\cdot}CH_2\cdot \ (O{-}O) \longrightarrow \cdot CH{\cdot}CH{:}CH\cdot \ (O{\cdot}OH)$$

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[57] *Bull. Soc. chim.*, 1945, **12**, 120.

[58] J. W. Lawrence and J. R. Shelton, *Ind. Eng. Chem.*, 1950, **42**, 136.

[59] Thesis, Fac Sci., Univ. Paris, 1943.

[60] U.S.P. 2,052,195 (Standard Oil Co.).

[61] (*a*) E. H. Farmer and D. A. Sutton, *J.*, 1943, 119; (*b*) C. E. Swift, F. G. Dollear, and R. T. O'Connor, *Oil & Soap*, 1946, **23**, 355.

[62] D. A. Sutton, *J.*, 1944, 242.

[63] F. D. Gunstone and T. P. Hilditch, *J.*, 1946, 1022.

During autoxidation of oleic acid, elaidic acid, and methyl oleate, an increase in ultra-violet absorption has been observed, probably through secondary formation of conjugated unsaturated ketones.[64]

Methyl methacrylate and vinyl acetate yield polymeric peroxides with oxygen.[65] Reduction of that from methyl methacrylate affords methyl $\alpha\beta$-dihydroxy*iso*butyrate suggesting that the peroxide system involved the carbon atoms originally carrying the double bond.

Pent-3-en-2-one on oxidation gives little peroxide ; the main reaction leads to fission of the molecule and production of acetaldehyde.[66]

Very little information is available on the reactions of olefin peroxides. Reduction of hex-1-ene hydroperoxide with sodium sulphite yielded hex-1-en-3-ol, indicating that the α-methylene group was that originally attacked.[54]

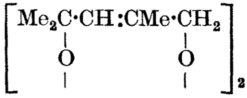
The reduction of the hydroperoxides of methyl oleate and methyl elaidate [61, 62] by a variety of means (aluminium amalgam, hydriodic acid, catalytic) has yielded methyl hydroxyoleate and then methyl hydroxystearate. Hydroxyoleic acid is also formed by action of alcoholic potash on the hydroperoxide,[61b] and permanganate oxidation leads to a mixture of octoic, pelargonic, suberic, and azelaic acids.

Hydroperoxides normally react with lead tetra-acetate to yield oxygen and the corresponding ketone.[67] It has been variously claimed that unsaturated olefin peroxides do [61b] and do not [68] give oxygen and ketones with the tetra-acetate ; the structure of this class of peroxide needs further resolving on the evidence of this reaction.

(2) *Polyolefins*.—The structure of many of the polyolefin peroxides is still in considerable doubt although suggestions have been made for some of the simpler ones. 2 : 3-Dimethylbutadiene and isoprene yield peroxides which on hydrogenation provide formaldehyde and a mixture of other decomposition products.[69] 2 : 4-Dimethylpenta-2 : 4-diene gives only a crude peroxide ; on heating at 80° this forms a dimer, $C_{14}H_{24}$, but at 100—120° a violent decomposition takes place to give formaldehyde, formic acid, and acetone. The structure proposed for the peroxide was : [70]

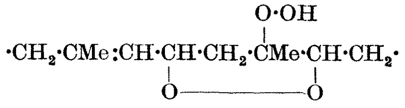
$$\begin{array}{l} Me_2C{\cdot}CH{:}CMe{\cdot}CH_2 \\ \quad\ | \qquad\qquad\quad\ | \\ \quad O\text{————}O \end{array}$$

or



$$\left[\begin{array}{l} Me_2C{\cdot}CH{:}CMe{\cdot}CH_2 \\ \qquad | \qquad\qquad\ | \\ \qquad O \qquad\quad\ \ O \\ \qquad | \qquad\qquad\ | \end{array}\right]_2$$

This may be compared with the diperoxide of squalene which appears to contain a hydroperoxide group and a cyclic peroxide in the system shown inset ; reduction leads to a triol containing an $\alpha\beta$-glycol system.[56b]



$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\quad O{\cdot}OH \\ \qquad\qquad\qquad\qquad\qquad\quad\ | \\ {\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{\cdot}CH_2{\cdot}CMe{\cdot}CH{\cdot}CH_2{\cdot} \\ \qquad\qquad\qquad\ \ | \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\ O\text{——————}O \end{array}$$

Peroxides from hepta-2 : 4-dien-6-one, mostly dimeric, have been made.[66]

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[64] R. T. Holman, W. O. Lundberg, W. M. Lauer, and G. O. Burr, *J. Amer. Chem. Soc.*, 1945, **67**, 1285.

[65] C. E. Barnes, R. M. Elofson, and G. D. Jones, *ibid.*, 1950, **72**, 210.

[66] H. Albers and W. Schmidt, *J. pr. Chem.*, 1943, **162**, 91.

[67] R. Criegee, H. Pilz, and H. Flygare, *Ber.*, 1939, **72**, 1799.

[68] W. Treibs, *ibid.*, 1944, **77**, 69. [69] K. Bodendorf, *Arch. Pharm.*, 1933, **271**, 1.

[70] R. Jacquemain, *Compt. rend.*, 1942, **215**, 200.

Autoxidation of methyl linoleate gradually takes place at 37°, accompanied by increased conjugation of the double bonds. Two peroxides are probably formed ; on hydrogenation one gives methyl 9- and 13-hydroxystearate (Geneva numbering), suggesting that the point of oxidation is at the methylene group between the double bonds, $C_{(11)}$, followed by rearrangement to a conjugated system, and the other peroxide yields a dihydroxystearic acid.[71] These results indicate that a cyclic peroxide as well as hydro-peroxide might well be produced during the oxidation.

The peroxide of methyl eleostearate on hydrogenation gave (*a*) lower aldehydes ; (*b*) methyl ω-formyloctoate, $OCH{\cdot}[CH_2]_7{\cdot}CO_2Me$; (*c*) a glycol, $C_{19}H_{38}O_4$, not an α-glycol ; (*d*) a trace of ester, $C_{19}H_{36}O_4$; and (*e*) a sodium carbonate-soluble saturated compound, $C_{19}H_{32}O_8$, which appeared to be a stable peroxide. The major products were (*b*) and (*c*), the latter probably being methyl 9 : 12-dihydroxystearate.[72]

Autoxidation of the system ·C:C·C·C:C·C·C:C· gave an increase in conjugation, and the extent of double-bond displacement seemed related to the degree of peroxidation.[73]

2. Alicyclic Peroxides

(**A**) **Cyclic Paraffin Peroxides.**—In general, hydroperoxides of this class have been made by oxidation of the corresponding hydrocarbon, although the reaction of tertiary alcohols with hydrogen peroxide and sulphuric acid has also been utilised.[23c, 26] Criegee has shown that the products are identical when prepared by both methods.

Oxidation of *cyclo*hexane normally gives rise to *cyclo*hexanone, *cyclo*hexanol, and adipic acid, but it is claimed [8,74] that at 316—328° this hydrocarbon yields two non-volatile peroxides, $C_4H_8O_4$ and $C_7H_{14}O_7$ (possibly $[HO{\cdot}O]_2{\cdot}C_6H_9{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$).

Recent patents [75] suggest that hydroperoxides of naphthenes may be obtained in concentrations up to 10% by oxidation in the presence of sodium carbonate or hydrogen carbonate ; presumably the carbonates remove acids formed during the oxidation and the presence of these acids would bring about decomposition of the peroxides. Some of the hydroperoxides so formed have been purified by concentration through their metal salts, and 1-methyl*cyclo*pentyl,[76] 1-methyl*cyclo*hexyl,[26,76, 77] and 1-ethyl*cyclo*hexyl hydroperoxide [26] have recently been prepared in a pure state.

During autoxidation of *cis*-decalin, a Walden inversion takes place with the formation of the *trans*-9-hydroperoxide.[78, 79]

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[71] S. Bergström, *Nature*, 1945, **156**, 717 ; *Arkiv Kemi, Min. Geol.*, 1945, **21**, *A*, No. 14, 1.

[72] W. Treibs, *Ber.*, 1943, **76**, 670.

[73] J. L. Bolland and H. P. Koch, *J.*, 1945, 445 ; E. H. Farmer, H. P. Koch, and D. A. Sutton, *J.*, 1943, 541.

[74] K. I. Ivanov, *J. Gen. Chem. Russia*, 1936, **6**, 470.

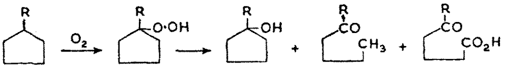
[75] U.S.P. 2,430,864, 2,430,865 (Union Oil).

[76] E. J. Gasson, E. G. E. Hawkins, A. F. Millidge, and D. C. Quin, in the press.

[77] K. I. Ivanov and V. K. Savinova, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **59**, 493.

[78] *Idem, Compt. rend. U.S.S.R.*, 1945, **48**, 31. [79] R. Criegee, *Ber.*, 1944, **77**, 22.

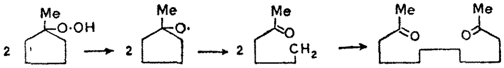
A difficulty connected with the formation of this class of hydroperoxide is that after a fairly low optimum concentration is reached, its decomposition to acids, ketones, and alcohols proceeds as rapidly as its formation.[76] Chavanne and his co-workers[80] studied the oxidation products of many substituted *cyclo*hexanes and *cyclo*pentanes and found that, in general, fission had occurred at the points of substitution to yield open-chain oxygenated compounds as well as cyclic alcohols :



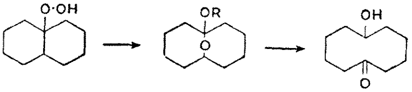
These compounds must have arisen from the initially formed hydroperoxides, although these were not isolated by Chavanne. With alkali these hydroperoxides yield metal salts which may be used for their concentration, but concentrated, warm alkali brings about decomposition in most cases.

The corresponding carbinols are produced smoothly by reduction with sodium sulphite or under catalytic conditions.[79]

A study of some of the reactions of methyl*cyclo*pentyl and methyl*cyclo*hexyl hydroperoxides has recently been carried out.[81] From methyl*cyclo*pentyl hydroperoxide the decomposition products given under a variety of conditions are mainly 1-methyl*cyclo*pentan-1-ol, methyl butyl ketone and 6-hydroxyhexan-2-one. A most surprising reaction is that of these two hydroperoxides with ferrous sulphate ; diketones with double the number of carbon atoms of the original hydroperoxide are formed in each case :[82]



Esters may be formed in the normal way by reaction with acid chlorides in the presence of pyridine, and tertiary hydroperoxides are esterified more easily than tertiary alcohols. *p*-Nitrobenzoates have been used as crystalline derivatives for the characterisation of several hydroperoxides.[26] An interesting rearrangement of the esters of decalin hydroperoxide in various solvents causes formation of an isomeric hemiacetal ; this on hydrolysis yields 6-hydroxy*cyclo*decan-1-one :[83]



Criegee has recently pointed out that the ease of rearrangement depends on

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[80] G. Chavanne, *Bull. Sci. Acad. roy. Belge*, 1926, **12**, 105 ; G. Chavanne, *Bull. Soc. chim. Belge*, 1927, **36**, 206 ; G. Chavanne and O. Miller, *ibid.*, 1930, **39**, 287 ; G. Chavanne and E. Bode, *ibid.*, p. 206 ; G. Chavanne and O. Miller, *ibid.*, 1931, **40**, 611 ; G. Chavanne, Mme. Pahlavouni and Mlle. Katzenstein, *ibid.*, p. 626 ; 1932, **41**, 209 ; G. Chavanne and G. Tock, *ibid.*, p. 630 ; P. Dupont and G. Chavanne, *ibid.*, 1933, **42**, 537.

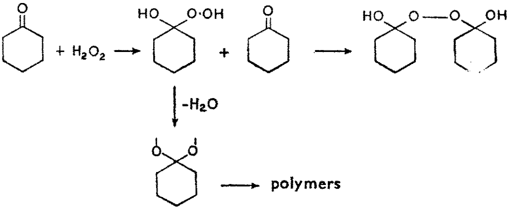
[81] E. G. E. Hawkins, in the press.

[82] E. G. E. Hawkins and D. P. Young, in the press.

[83] R. Criegee, *Ber.*, 1944, **77**, 722 ; *Annalen*, 1948, **560**, 127.

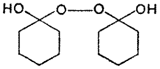
(i) the strength of acid used in esterification, (ii) hydroperoxide structure, and (iii) the solvent.

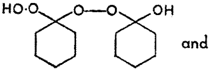
Hydroxy*cyclo*alkyl hydroperoxides and di(hydroxy*cyclo*alkyl) peroxides are formed by reaction of cyclic ketones with hydrogen peroxide, similarly to the comparable reaction with the open-chain carbonyl compounds ; [84] *e.g.*,



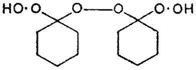
These hydroxy-hydroperoxides are highly explosive and on dehydration yield polymeric peroxides.

However, in a recent paper R. Criegee, W. Schnorrenberg, and J. Becke [85] have shown that the peroxides formed from *cyclo*hexanone and hydrogen peroxide are actually :

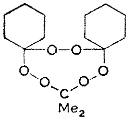

(IV)

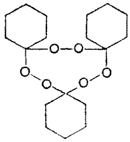


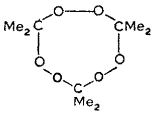
(V)


(VI)

On condensing (VI) with acetone and *cyclo*hexanone the compounds (VII) and (VIII), respectively, are given :


(VII)


(VIII)


(IX)

From the ease of formation of these compounds the authors conclude that the cyclic formula (IX) for the trimeric acetone peroxide is probably correct.

In a recent communication Criegee [26] claims to have obtained the 1 : 1 : 6 : 6-tetrahydroperoxide (X) of *cyclo*decane by treatment of *cyclo*decane-1 : 6-dione with hydrogen peroxide.

(B) Cyclic Olefin Peroxides.—These peroxides have been produced by treatment of the cyclic olefins with air or oxygen, followed by final separation from the other products and unchanged olefin. *cyclo*Pentenyl hydroperoxide has been prepared by this means,[67] but much more study has been

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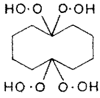
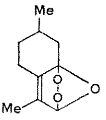
[84] N. A. Milas, S. A. Harris, and P. C. Panagiotakos, *J. Amer. Chem. Soc.*, 1939, **61,** 2430; U.S.P. 2,298,405 (Research Corp.).

[85] *Annalen,* 1949, **565,** 7.

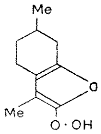
devoted to *cyclo*hexenyl hydroperoxide.[67, 86] Hydroperoxides of 1-methyl*cyclo*hexene,[67, 86e, 87] 1: 2-dimethyl*cyclo*hexene,[86e, 87] menthene,[88] α-phellandrene, *cyclo*hexadiene, and α-terpinene [69] have been similarly prepared, and it has been stated that dimethyl-, methylethyl-, and phenylmethyl-fulvenes yield diperoxides.[89] It has been suggested that the keto-alcohol obtained by oxidation of menthofuran [90] arises *via* a cyclic peroxide (XI) or a hydroperoxide (XII).



(X)

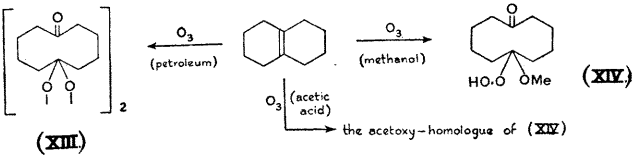


(XI)



(XII)

Ozonolysis of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydronaphthalene has given complex peroxides,[91] the actual peroxide formed depending on the solvent used for the ozonolysis.



(XIII)

(XIV)

Thermal decomposition of *cyclo*hexenyl hydroperoxide at 70—80° gives *cyclo*hexenol, but, when it is heated with water, *cyclo*pentenealdehyde is also produced as well as small quantities of *cyclo*hexanetriol and acid.[86e]

H. Hock and O. Schräder [86b, c] state that dilute sulphuric acid reacts with *cyclo*hexenyl hydroperoxide to yield *cis*-*cyclo*hexane-1 : 2-diol and *cyclo*pentenealdehyde. However, a careful study of the decomposition of this hydroperoxide and those from various substituted *cyclo*hexenes with acid by Farmer *et al.*[86e] has shown it to give the corresponding triol as well as the unsaturated alcohol and a little *cyclo*pentenecarbonyl derivative. These products may possibly arise by the sequence of reactions shown on the next page.

Reaction (iv) to give *cyclo*pent-1-en-1-al is parallel to that of the acid decomposition of the hydroperoxide of decalin.[83]

Alkali reacts with these hydroperoxides to give as main product the corresponding unsaturated alcohol, and, in addition, some acids.[86] A study

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[86] (*a*) H. N. Stephens, *J. Amer. Chem. Soc.*, 1928, **50,** 568; (*b*) H. Hock and O. Schräder, *Naturwiss.*, 1936, **24,** 159; (*c*) *idem, Z. angew. Chem.*, 1936, **49,** 565; (*d*) H. Hock and K. Gänicke, *Ber.*, 1938, **71,** 1430; (*e*) E. H. Farmer and A. Sundralingam, *J.*, 1942, 121; (*f*) N. D. Zelinski and P. P. Borisov, *Ber.*, 1930, **63,** 2362.

[87] E. H. Farmer and D. A. Sutton, *J.*, 1946, 10.

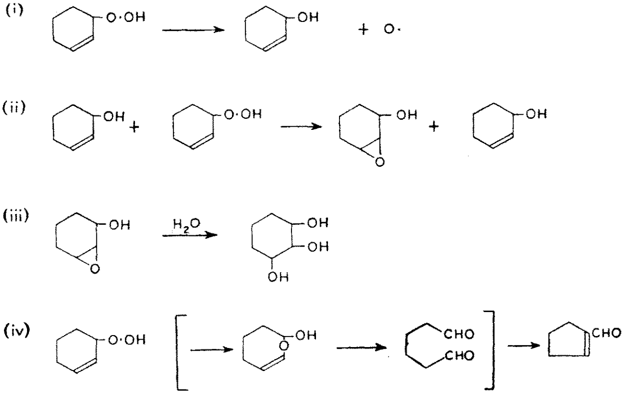
[88] H. Hock, and S. Lang, *Ber.*, 1942, **75,** 300.

[89] C. Engler and W. Frankenstein, *ibid.*, 1901, **34,** 2933.

[90] R. B. Woodward and R. H. Eastman, *J. Amer. Chem. Soc.*, 1950, **72,** 399.

[91] R. Criegee and G. Wenner, *Annalen*, 1949, **564,** 9.

of the acid products from *cyclo*hexenyl hydroperoxide showed the presence of formic, acetic, glutaric, adipic, (mainly) α-hydroxyadipic, and higher-boiling acids. Many of the shorter-chain acids must have arisen through degradation, but the α-hydroxyadipic acid may well have come by fission of a C–C link of the triol.



On catalytic reduction the expected saturated alcohol is given. *cyclo*Hexenyl hydroperoxide gives *cyclo*hexanol, and 1-methyl*cyclo*hexenyl hydroperoxide provides both 3- and 2-methyl*cyclo*hexanol (owing to the presence of the 6- and the 3-hydroperoxide). α-Terpinene and α-phellandrene peroxides both yield diols on hydrogenation, and *cyclo*hexadiene peroxide is reduced slowly to *cis*- and *trans*-quinitol.

Sodium sulphite brings about reduction of cyclic olefin hydroperoxides to the corresponding unsaturated alcohols ; the hydrogen sulphite (pyrosulphite) reacts rather more vigorously, and with menthene hydroperoxide it gives rise to mentha-1 : 3-diene in addition to the unsaturated alcohol.[92]

Catalysts such as ferrous phthalocyanine lead to an exothermic decomposition to yield the enones and enols.[86e] Lead tetra-acetate causes liberation of oxygen.[67]

*cyclo*Hexene and menthene hydroperoxides have been methylated with methyl sulphate and sodium hydroxide at controlled pH ; yields of 40—70% of the methyl peroxide are recorded.[88] Diazomethane cannot be used for the methylation of these compounds.

(C) Peroxides from Partly Reduced Aromatic Hydrocarbons.—Preparation of these hydroperoxides has again been limited to the method of controlled air oxidation of the hydrocarbon. The most extensively studied member of this series is the hydroperoxide of tetralin ; [93, 94] the

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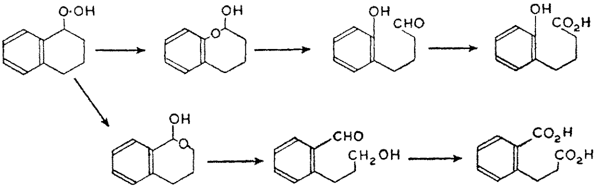
[92] H. Hock and S. Lang, *Ber.*, 1942, **75**, 313.

[93] M. Hartmann and M. Seiberth, *Helv. Chim. Acta*, 1932, **15**, 1390 ; U.S.P. 1,924,786 ; B.P. 396,351.

[94] (*a*) H. Hock and W. Susemihl, *Ber.*, 1933, **66**, 61 ; (*b*) W. Nussle, G. W. Perkins, and G. Toennies, *Amer. J. Pharm.*, 1935, **107**, 29 ; (*c*) K. I. Ivanov, V. K. Savinova, and E. G. Mikhailova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **25**, 34 ; (*d*) A. Robertson and W. A. Waters, *J.*, 1948, 1574, 1578, 1585.

hydroperoxides of indane [95] and octahydroanthracene [96] have also been isolated.

The presence of tetralone and ditetralyl peroxide was detected during the oxidation of tetralin; [97] the ketone and tetralol have also been found in the products of thermal decomposition of the hydroperoxide.[93] Other products obtained by thermal treatment were dihydronaphthalene, γ-*o*-hydroxyphenylbutyraldehyde, γ-*o*-hydroxyphenylbutyric acid, and β-*o*-carboxyphenylpropionic acid; [94d] the first acid has also been isolated in small quantities from the acid-treated hydroperoxide.[98] The aldehyde and the acids may well be produced by a mechanism similar to that suggested by Criegee for decalin peroxide → hydroxy*cyclo*decanone.



Alkali reacts in the normal way with these hydroperoxides; with cold alkali the sodium salts are given but, on heating, the hydroperoxide is converted into ketone or alcohol or a mixture of both.[94a, 95] Tetralyl hydroperoxide provides mainly tetralone (70%), whereas the indane compound gives indan-1-ol (55%) and a little indan-1-one (5%).

Reduction with sodium sulphite yields the corresponding alcohol in every case; [92] the pyrosulphite, however, causes some dehydration of α-tetralol to di-α-tetralyl ether and dihydronaphthalene.

Permanganate oxidation of tetralyl hydroperoxide gives rise to β-*o*-carboxyphenylpropionic acid,[94a] and free oxygen brings about decomposition of octahydroanthryl hydroperoxide to the ketone.[96]

Reaction of a benzene solution of formaldehyde with tetralyl hydroperoxide affords tetralyl hydroxymethyl peroxide; the normal ether solvent used in this type of reaction gives no satisfactory product.[99]

As in the case of the cyclic olefin hydroperoxides, methylation by means of methyl sulphate and alkali proceeds smoothly.[88, 95]

All these hydroperoxides lose water on catalytic treatment (ferrous sulphate; [93, 95, 96] lead tetra-acetate; [95] metal phthalocyanines [100]) to give good yields of the corresponding ketones.

Tetralyl hydroperoxide has been used as an oxidising agent for various olefins in the presence of an osmium tetroxide catalyst; [101] for instance, 1 : 2-dimethyl*cyclo*hexene was converted into octane-2 : 7-dione.

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[95] H. Hock and S. Lang, *Ber.*, 1942, **75**, 1051. [96] *Idem, ibid.*, 1943, **76**, 1130.

[97] S. S. Medvedev, *Acta Physicochim. U.S.S.R.*, 1938, **9**, 405.

[98] H. Hock and S. Lang, *Ber.*, 1944, **77**, 257.

[99] K. I. Ivanov, V. K. Savinova, and E. G. Mikhailova, *J. Gen. Chem. Russia*, 1938, **8**, 51.

[100] J. H. Helberger and D. B. Hever, *Ber.*, 1939, **72**, 11.

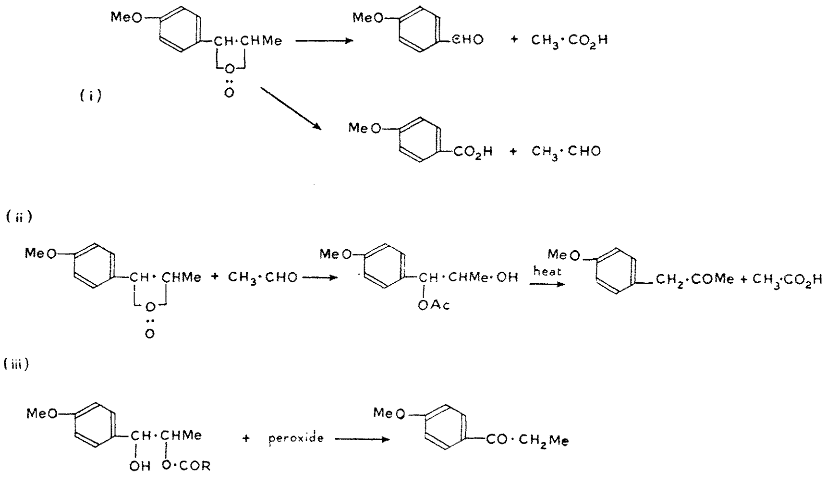
[101] T. Cosciug, *Ann. sci. Univ. Jassy*, Sec. I, 1941, **27**, 303.

(D) **Aralkyl Peroxides.**—(1) *Hydroperoxides.*—Air oxidation of hydrocarbons is again the normal mode of formation, although triphenylmethyl hydroperoxide at least appears to have been formed by reaction of triphenylmethyl chloride with hydrogen peroxide.[102] Various alkylbenzenes oxidised at 100—102° gave peroxides in quantity corresponding to 60—80% of the oxygen consumed.[22] Passage of oxygen through the heated hydrocarbon, either as a homogeneous phase or in emulsion, has been used to prepare the hydroperoxides of cymene,[103] *p*-xylene,[104] diphenylmethane,[98] *iso*propylbenzene,[99, 105] and *sec.*-butylbenzene,[106] and the dihydroperoxides of di*iso*propylbenzene (*m*- and *p*-isomers).[107]

It has been found that oxidation of various substituted benzenes (ethyl-, *sec.*-butyl-, *sec.*-amyl-, *sec.*-hexyl-) yielded acetophenone, whilst others (*as*-diphenylethane, diphenylmethane, and triphenylmethane) similarly gave benzophenone, all presumably through the hydroperoxides.[108]

The oxidation of various alkylbenzenes at higher temperatures (100—650°) has been studied, and it is stated that both *iso*propyl- and *tert.*-butyl-benzene yield phenol and acetone.[109]

Anethole on oxidation yields a mixture of anisaldehyde, anisic acid, acetic acid, a ketol, and a glycol, as well as dimeric autoxidation products. The mechanism suggested [110] for the production of these compounds involves the reaction of an intermediate cyclic peroxide similar to those mentioned by Paquot for aliphatic olefins:



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[102] H. Wieland and J. Maier, *Ber.*, 1931, **64,** 1205.

[103] J. H. Helberger, A. Rebay, and H. Fettback, *ibid.*, 1939, **72,** 1643.

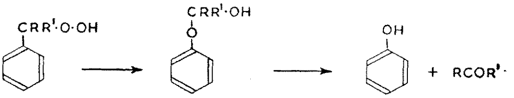
[104] H. Hock and S. Lang, *ibid.*, 1943, **76,** 169.

[105] B.P. 610,293, 629,637, 630,286 (Distillers Co. Ltd.); G. P. Armstrong, R. H. Hall, and D. C. Quin, *Nature,* 1949, **164, 834**; *J.*, 1950, **66.**

[106] (*a*) K. I. Ivanov, V. K. Savinova, and V. P. Zhakhovskaya, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **59,** 905; (*b*) E. G. E. Hawkins, *J.*, 1949, 2076; (*c*) E. G. E. Hawkins, in the press; (*d*) I. M. Kolthoff and A. I. Medalia, *J. Amer. Chem. Soc.*, 1949, **71,** 3789.

The products of oxidation also include compounds formed by demethylation, nuclear oxidation to phenols, and nuclear degradation.

Acid leads to production of a phenol and a carbonyl compound from those hydroperoxides studied, possibly through the hemiacetal rearrangement :



For instance diphenylmethyl hydroperoxide yields phenol and benzaldehyde, whereas phenol and acetone are formed from αα-dimethylbenzyl hydroperoxide (from *iso*propylbenzene), phenol and methyl ethyl ketone from the *sec.*-butylbenzene homologue, and quinol and acetone from *p*-αα'α'-tetramethylxylylene dihydroperoxide (from *p*-di*iso*propylbenzene).

Alkali appears to give rise to the corresponding carbonyl derivative, although the metal salt of the hydroperoxide is first formed. It has been stated [103] that the hydroperoxide from cymene yields cuminaldehyde, although this infers that oxidation has taken place at the primary rather than the expected tertiary carbon atom. That from *p*-xylene gives *p*-tolualdehyde, which by a Cannizzaro reaction is converted into tolylcarbinol and toluic acid.[104]

All the hydroperoxides of this class are smoothly reduced to the alcohol by sodium sulphite. Reduction has also been carried out by hydrogenation or by the use of alkali metal sulphides.[111]

Decomposition of the hydroperoxides of ethylbenzene, *iso*propylbenzene, and *sec.*-butylbenzene with ferrous sulphate leads in each case to acetophenone.[104, 106] The physical chemistry of the reaction of the ferrous ion with the hydroperoxide of cumene has been studied in detail.[106d] Thermal and catalytic decomposition of αα-dimethylbenzyl hydroperoxide has been shown to yield a mixture of acetophenone, 2-phenylpropan-2-ol and α-methylstyrene.[106c]

Triphenylmethyl hydroperoxide is unaffected by ferrous sulphate ; with benzoyl chloride it yields an isomer of the expected benzoate, probably $Ph_2C(OPh)OBz$, since with alcoholic potash phenol, benzoic acid, and benzophenone are obtained.[102] This is yet another case of rearrangement of a hydroperoxide or its ester to a hemiacetal.

It has been shown [106c] that αα-dimethylbenzyl hydroperoxide may act as a mild oxidising agent especially in the presence of catalysts ; aldehydes may be oxidised to acids, secondary alcohols to ketones and even olefins converted into various oxygenated products.

(2) *Peroxides* (RO·OR).—Many of these have been described in the

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[107] E. G. E. Hawkins and D. C. Quin, unpublished.

[108] H. N. Stephens, *J. Amer. Chem. Soc.*, 1926, **48,** 2920 ; H. N. Stephens and F. L. Roduta, *ibid.*, 1935, **57,** 2380.

[109] S. Tonomura, *Bull. Inst. Phys. Chem. Res.* (*Tokio*), 1942, **21,** 774.

[110] L. Schulz and W. Treibs, *Ber.*, 1944, **77,** 377.

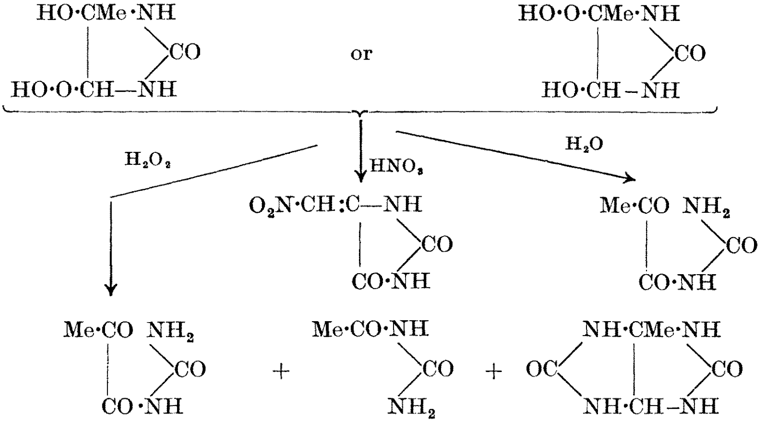
[111] U.S.P. 2,491,926, 2,484,841 (Hercules Powder Co.).

literature and no attempt is made here to list them. In many cases, however, they have been prepared but their reactions not studied. One of the procedures most frequently adopted for their preparation has been that of treating a tertiary halide with finely divided metal (*e.g.*, zinc, silver, mercury) in the presence of air or oxygen. These peroxides have been prepared by a variety of workers, although Marvel and his co-workers (1935—44) in America and Bowden *et al.* (1939—40) in Wales have contributed to a large extent in this field.

Several diaryl ketone peroxides have been prepared by ozonolysis of unsaturated systems, *e.g.*, $Ph_2C{:}CH_2 \longrightarrow$ benzophenone peroxide, and $(p\text{-}MeC_6H_4)_2C{:}CHMe \longrightarrow$ di-*p*-tolyl ketone peroxide.[112]

3. Peroxides of Heterocyclic Compounds

It has been known [113] for a considerable time that the condensation product of urea and methylglyoxal formed a peroxide on treatment with hydrogen peroxide and ferrous sulphate. This peroxide underwent the following reactions :



Like open-chain ethers, cyclic acetals and ketals will peroxidise in air,[114] and peroxides of dioxans and dioxolans have been made in dilute solution for use as polymerisation catalysts.[115]

The dimerisation product of methyl vinyl ketone (probably 6-acetyl-2-methyl-5 : 6-dihydro-1 : 4-pyran) forms a peroxide on treatment with hydrogen peroxide and acetic acid.[116]

Peroxides of tetrahydrofuran and its alkyl-substituted homologues are formed by low-temperature autoxidation (25—40°) ; [117] peroxides of furan

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[112] *Inter alii*, C. S. Marvel and V. E. Nichols, *J. Amer. Chem. Soc.*, 1938, **60**, 1455 ; *J. Org. Chem.*, 1941, **6**, 296.

[113] L. Seekles, *Rec. Trav. chim.*, 1927, **46**, 77.

[114] M. Kuhn, *J. pr. Chem.*, 1940, **156**, 103.

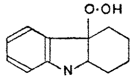
[115] B.P. 586,146 (Usines de Melle).

[116] K. Alder, H. Offermanns, and E. Rüden, *Ber.*, 1941, **74**, 905.

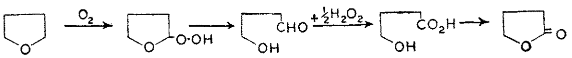
[117] (*a*) B.P. 532,158, 614,392 (Usines de Melle) ; (*b*) A. Robertson, *Nature*, 1948, **162**, 153.

and 2 : 5-dimethylfuran [118] have been prepared similarly, the speed of oxidation being increased by illumination or addition of catalysts ($CaCl_2$, $FeSO_4$, $NiSO_4$, $MnSO_4$).

Recently, it has been found that tetrahydrocarbazole and its homologues yield peroxides on autoxidation ; [119] these are probably of the type shown inset.



γ-Butyrolactone may be prepared by direct oxidation of tetrahydrofuran in the presence of catalysts [120] and it is also a product of the decomposition of tetrahydrofuryl hydroperoxide.[117b] On the other hand, it has also been claimed [115, 117a] that this hydroperoxide and its alkyl homologues are decomposed by acid or alkali to afford a γ-aldol or γ-ketol and hydrogen peroxide. Presumably, butyrolactone is formed as the result of further reaction of the hydrogen peroxide with the hydroxybutanal followed by dehydration of the hydroxybutyric acid :



Furyl peroxide resinifies on storage, and reduction over palladium-barium sulphate gives 30—40% of succindialdehyde. 2 : 5-Dimethylfuryl peroxide is similarly reduced to hexane-2 : 5-dione.[104] The autoxidation products of 2-methylfuran and tetraphenylfuran have been studied in a similar way.[121]

Autoxidised 2 : 5-dimethylfuran when cooled to — 80° deposits crystals of hex-3-ene-2 : 5-dione, and when the speed of oxidation is increased by use of one of the catalysts mentioned above the yield of diketone is increased to 50%. In general,[122]

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[118] G. O. Schenck, *Naturwiss.*, 1943, **31**, 387 ; *Ber.*, 1944, **77**, 661.

[119] R. J. S. Beer, L. McGrath, A. Robertson, and A. B. Woodier, *Nature*, 1949, **164**, 363.

[120] B.P. 608,539 (I.C.I.).

[121] G. O. Schenck, *Angew. Chem.*, 1948, **60**, 244.

[122] *Idem*, *Chem. Ber.*, 1947, **80**, 289.