dibenzoyl derivative of 1-isopropylamino-2,2-dimethyl-2-aminoethane with m.p. 146°. It gave a mixed m.p. 146° with an authentic sample. (Riebsomer[1] gives m.p. 146°–147°.)

Attempted acetylation of an imidazolidine. N_1-isopropyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethyl-imidazolidine (III, R_1 = *i*-Pr, R_2 = H, R_3 = R_4 = Me) was treated with acetyl chloride under the usual conditions for acetylating an amine. No solid product could be isolated. The mixture, even −10°, formed a sticky tar which decomposed on attempted distillation.

Attempted hydrogenation of an imidazolidine using sodium and ethanol. To a solution of N_1-phenyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethyl-imidazolidine (III, R_1 = Ph, R_2 = H, R_3 = R_4 = Me) (29.6 g.) in very dry ethanol[11] (250 ml.) was added sodium (9.2 g.) in large pieces at such a rate that a vigorous reflux was maintained. When all the sodium had been added and the reaction began to subside, the mixture was heated under gentle reflux till the last traces of sodium dissolved (30 min.). The mixture was cooled and poured on to ice (250 g.) and the alcohol removed under reduced pressure at 40°. On cooling white crystals (27.3 g.) were formed, which after purification melted at 102°. Mixed m.p. with starting material 102°; showing that only the unchanged starting material could be recovered.

Acknowledgment. The author is pleased to express his appreciation to the Research Laboratory of Commercial Solvents Corporation for the generous gift of samples of some of the 1,2-diamines used in this investigation.

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[11] H. Lund and J. Bjerrum, *Ber.*, 64B, 210 (1931).

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF CHICAGO]

Metal Salt–Induced Homolytic Reactions. I. A New Method of Introducing Peroxy Groups into Organic Molecules[1,2]

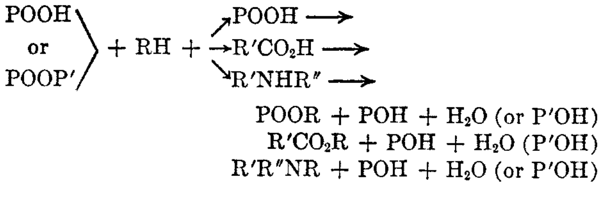
M. S. KHARASCH[3] AND ANDREW FONO[4]

Received July 30, 1958

A new and general method for the introduction of alkyl and aralkyl peroxy groups (ROO) into many types of organic molecules has been developed. This is accomplished by the use of a hydroperoxide and a copper, cobalt, or manganese salt catalyst. The versatility of this method is indicated by the fact that compounds of such diverse structure as cyclohexene, octene-1, cumene, α-methylcyclohexanone, cyclohexanone, dimethylaniline, xylene, and dioxane give good to excellent yields of the unsymmetrical peroxides.

Work done at this laboratory indicates that the metal-induced reaction of a hydroperoxide with organic compounds is as effective in introducing ROO groups as *N*-bromosuccinimide is in introducing bromine atoms into organic molecules. The two reactions are similar as both require an initiator and proceed by a free radical chain reaction. This similarity does not hold for the reactions in which the bromination by *N*-bromosuccinimide proceeds by an ionic mechanism, *e.g.*, the nuclear bromination of aromatic compounds.

Subsequent publications will extend this reaction to the introduction of acyloxy and imido groups:



$$\left.\begin{matrix}\text{POOH}\\ \text{or}\\ \text{POOP}'\end{matrix}\right\rangle + \text{RH} + \begin{matrix}\nearrow\text{POOH} \longrightarrow\\ \rightarrow\text{R}'\text{CO}_2\text{H} \longrightarrow\\ \searrow\text{R}'\text{NHR}'' \longrightarrow\end{matrix}$$

$$\begin{matrix}\text{POOR} + \text{POH} + \text{H}_2\text{O (or P}'\text{OH)}\\ \text{R}'\text{CO}_2\text{R} + \text{POH} + \text{H}_2\text{O (P}'\text{OH)}\\ \text{R}'\text{R}''\text{NR} + \text{POH} + \text{H}_2\text{O (or P}'\text{OH)}\end{matrix}$$

All of these reactions are promoted by copper salts, but most of them occur, to some extent, even in their absence. This study deals with reactions where the main function of the metal salts is only to initiate the decomposition of the hydroperoxides. Subsequent publications will discuss reactions where the metal salts also react with the free radicals initially formed, to alter the course of the reaction.

It has been previously shown that:

(*a*) If reactive free radicals are generated in a solution of *tert*-butyl hydroperoxide in cumene, *tert*-butyl-α-cumyl peroxide is formed. The free radicals were generated by the termal decomposition of acetylperoxide.[5a]

(*b*) Cobalt salts catalyze the decomposition of hydroperoxides, causing the formation of reactive free radicals.[5b]

(*c*) In the presence of a reactive substrate like cyclohexene[5c] or tetralin,[5d] cobalt salts catalyze the reaction of the hydroperoxides with the substrate to form peroxides.

The present work indicates that by careful choice of the catalyst and the reaction conditions, these reactions can be made very general and almost quantitative.

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[1] Previous communication, M. S. Kharasch and A. Fono, *J. Org. Chem.*, 23, 324 (1958).

[2] This work was made possible through the generous support of O. B. May, Inc. Newark, N. J.

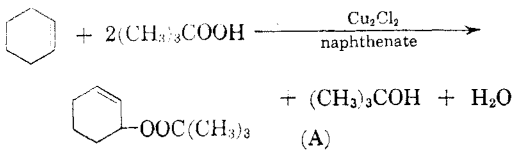
[3] Deceased.

[4] Present address: Firestone Chemical and Physical Research Laboratories, Akron, Ohio.

[5] (a) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, 15, 753 (1950). (b) M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, 17, 207 (1952). (c) M. S. Kharasch, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, 18, 322 (1953). (d) W. Treibs and G. Pellmann, *Ber.*, 87, 1201 (1954).

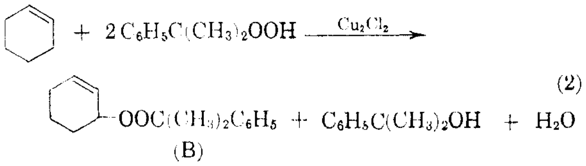
RESULTS

Reaction of tert-butyl hydroperoxide and α-cumyl hydroperoxide with cyclohexene in the presence of cuprous chloride. It was shown that, in the presence of small amounts of cobaltous naphthenate, *tert*-butyl hydroperoxide reacts with cyclohexene, or with octene-1 to give unsymmetrical peroxides.[5c] The yield of 1-*tert*-butylperoxycyclohexene (A), on the basis of the hydroperoxide used was approximately 60%. Much of the hydroperoxide decomposed by chain reaction into oxygen and *tert*-butyl alcohol. Present work indicates that the amount of oxygen liberated in the reaction may be considerably decreased by adding the cobalt salt very slowly. The hydroperoxide is used more efficiently in the presence of cuprous chloride.

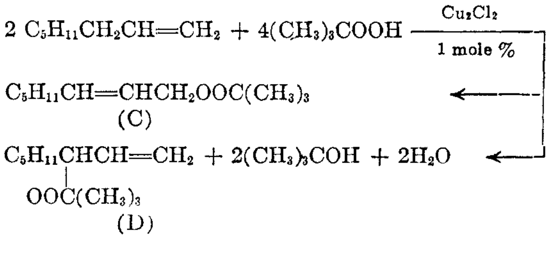


(1)

When 1 mole % of cuprous chloride was added to a mixture of cyclohexene and α-cumyl hydroperoxide (on the basis of the peroxide used), and this mixture kept at 70° for 20 hr., the yield of the unsymmetrical peroxide B was nearly quantitative. This peroxide is quite stable and may be distilled without decomposition at reduced pressure (90°/0.1 mm.). Based on infrared spectrum, analysis, and anology, structure B is suggested.



Reaction of tert-butyl hydroperoxide with octene-1 in the presence of cuprous chloride. When a mixture of *tert*-butyl hydroperoxide and octene-1 is heated at 75° for 14 hr., only a small amount of the hydroperoxide was decomposed. However, in the presence of one mole % of cuprous chloride, 80% of the hydroperoxide was decomposed at 70° in 6 hr. The reaction products were *tert*-butyl alcohol and about equal quantities of C and D, 1-*tert*-butylperoxyoctene-2 and 3-*tert*-butylperoxyoctene-1, respectively. The same reaction occurred when instead of a copper salt, a cobalt salt was used as a catalyst.



$$2\,C_5H_{11}CH_2CH{=}CH_2 + 4(CH_3)_3COOH \xrightarrow[\text{1 mole \%}]{Cu_2Cl_2}$$

$$\underset{\text{(C)}}{C_5H_{11}CH{=}CHCH_2OOC(CH_3)_3}$$

$$\underset{\text{(D)}}{\underset{OOC(CH_3)_3}{C_5H_{11}\underset{|}{C}HCH{=}CH_2}} + 2(CH_3)_3COH + 2H_2O \qquad (3)$$

When to a mixture of *tert*-butyl hydroperoxide and octene-1 very small amounts (0.2 mole %) of cobalt-2-ethylhexoate (dissolved in octene-1) were added at 65–70° over a period of 2 hr., peroxides C and D were again formed in equal quantities. The fractions containing a mixture of peroxides C and D obtained from the copper and the cobalt salt catalyzed reactions were identical with each other in all physical properties (index of refraction, boiling point and infrared spectrum).[6]

Peroxides C and D, the components of the reaction mixture were separated by distillation, using a Piros-Glover spinning band column. The fractions to which structures D and C were assigned boiled at 57°/2.5 mm. (n_D^{20} 1.4243), and 72°/2.5 mm. (n_D^{20} 1.4320) respectively. The infrared spectrum of C with a band at 970 cm.$^{-1}$,[7] indicated the presence of a nonterminal (*trans*) bond. The infrared spectrum of D (bands at 920 cm.$^{-1}$ and 990 cm.$^{-1}$) indicates the presence of a terminal double bond.[8] The infrared spectra of C and D suggest that they probably do not contain more than 5% of each other. A 50–50 mixture of C and D showed an identical infrared spectrum with the crude peroxide isolated from the reaction.

Reaction of tert-butyl hydroperoxide with cumene in the presence of cuprous salts. A solution of *tert*-butyl hydroperoxide in cumene is stable when heated to 70° for 24 hr. However, if 1 mole % of cuprous chloride is added to this solution, and the combined mixture heated to 67° for 18 hr., about 80% of the hydroperoxide is decomposed, according to the stoichiometric reaction 4.

$$C_6H_5(CH_3)_2CH + 2(CH_3)_3COOH \xrightarrow[\text{1 mole \%}]{Cu_2Cl_2}$$

$$\underset{\text{(E)}}{C_6H_5C(CH_3)_2OOC(CH_3)_3} + (CH_3)_3COH + H_2O \qquad (4)$$

The *tert*-butyl-α-cumyl peroxide E obtained has the same physical constants (b.p. 60°/2 mm.; n_D^{20} 1.4800) as the *tert*-butyl-α-cumyl peroxide prepared from either *tert*-butyl hydroperoxide and dimethylphenylcarbinol (α-cumyl alcohol),[9] or from cumene, *tert*-butyl hydroperoxide, and acetyl peroxide.[10]

Cupric chloride, cuprous and cupric bromide, cuprous and cupric benzoate were found to be just as effective catalysts as cuprous chloride.

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(6) The apparent difference in the abundance of the isomers of C and D observed here, and by Kharasch, Pauson, and Nudenberg [*J. Org. Chem.*, **18**, 322 (1953)] is to be ascribed to the fact that better fractionating columns are now in use.

(7) There is an additional strong band at 1017 cm.$^{-1}$

(8) Note that a similar shift of the band from 910 cm.$^{-1}$ to 920 cm.$^{-1}$ was noted in the infrared spectrum of 3-bromooctene-1 [M. S. Kharasch, R. Malec, and N. C. Yang, *J. Org. Chem.*, **22**, 1443 (1957)].

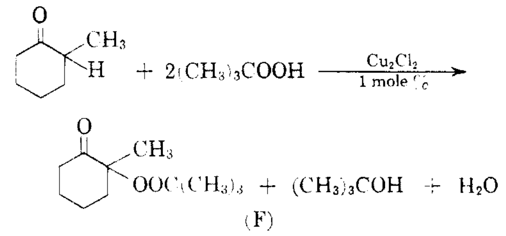
(9) M. S. Kharasch, A. Fono, W. Nudenberg, and A. C. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).

(10) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 753 (1950).

The same peroxide was also obtained, when instead of excess cumene, benzene or chloroform, or heptane or *tert*-butyl alcohol, or pyridine, or acetic acid, or nitrobenzene, or ethyl acetate was used as a solvent. These solvents were also found to be suitable for the preparation of the other peroxides reported here.

A good yield of *tert*-butyl-α-cumyl peroxide E was also obtained by heating a mixture of cumene, *tert*-butyl hydroperoxide, and cobalt 2-ethylhexoate (0.2 mole %) to 65–70°. The cobalt salt was dissolved in cumene and added, drop by drop, over a period of 3 hr. The only difference noted when cobalt salts were used instead of cuprous salts, was the formation of large amounts (30%) of dimethylphenylcarbinol.[11] The best yield, 92%, of pure *tert*-butyl-α-cumyl peroxide was obtained when acetic acid was used as a solvent, and manganous bromide was substituted for the cuprous or cobaltous salt.

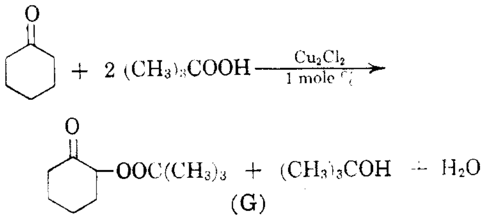
Reactions of 2-methylcyclohexanone and of cyclohexanone with tert-butyl hydroperoxide in the presence of cuprous salts. A mixture of 2.5 moles of 2-methylcyclohexanone, 1 mole of *tert*-butyl hydroperoxide, and 1 mole % of cuprous chloride was heated to 60° for 7 hr. 75% of the hydroperoxide had decomposed at the end of that time, and a practically quantitative yield of the unsymmetrical peroxide, on the basis of the hydroperoxide consumed, was obtained. Based on infrared spectrum, analysis, and anology, structure F is suggested.



(5)

The infrared spectrum of 2-methyl-2-*tert*-butylperoxycyclohexanone (F) showed bands in the carbonyl region at 1722–1725 cm.$^{-1}$ 2-methylcyclohexanone has a band at 1705–1710 cm.$^{-1}$ The shift was attributed to the presence of an electro negative substituent in the 2 position. Compound F also had bands at 1370 cm.$^{-1}$ (strong) and 1390 cm.$^{-1}$ (medium) which indicated the presence of a *tert*-butyl group. Bands at 1198 cm.$^{-1}$ and 888 cm.$^{-1}$ were attributed to the presence of the *tert*-butoxy group.

In the presence of 1 mole % cuprous chloride, the reaction of cyclohexanone with *tert*-butyl hydroperoxide gave many products: adipic acid, the half-aldehyde of adipic acid, and approximately 20% of the unsymmetrical peroxide, 2-*tert*-butylperoxycyclohexanone (G). Left to stand, peroxide G slowly decomposes. Therefore, we felt it plausible to assume that G is a primary reaction product and that other compounds arose from the thermal decomposition of G, in the presence of the *tert*-butyl hydroperoxide and the cuprous (or cupric) salt.



(6)

An infrared spectrum of a freshly prepared sample of G shows bands at 1368 cm.$^{-1}$ (strong) and 1390 cm.$^{-1}$ (medium), indicating the presence of the *tert*-butyl group. Bands at 875 cm.$^{-1}$ (medium) and 1200 cm.$^{-1}$ (medium) are attributed to the presence of the *tert*-butoxy group. A band at 1720 cm.$^{-1}$ (strong) is accredited to the carbonyl group. Note the shift caused by an α substituent. Cyclohexanone has a band in the carbonyl region at 1710 cm.$^{-1}$ The same shift in wave length has been observed in cyclohexanones halogenated in the 2-position.

Reactions of dimethylaniline with tert-butyl hydroperoxide in the presence of cuprous salts. Because it is a strong base, several attempts to attack dimethylaniline by free radicals have failed. It can be brominated by *N*-bromosuccinimid, giving *p*-bromodimethylaniline in 75% yields.[12] However, it has been shown[13] that this is an ionic and not a free radical reaction. When benzoyl peroxide was decomposed in dimethylaniline,[14] the product *o,o'*-bis(dimethylamino)diphenyl amine again seemingly arose through an ionic mechanism. The reaction was not influenced by the presence of copper salts. Nitrogen is known to activate a neighboring carbon-hydrogen bond[15] and we expected that free radicals should preferentially attack the methyl groups of dimethylaniline.

When we added 1 mole % cuprous chloride to an equimolar mixture of dimethylaniline and *tert*-butyl hydroperoxide dissolved in benzene, the reaction mixture proceeded to heat up. It was maintained at 35°. After 12 hr., the iodometric titer in acidic acid dropped to one half of its original value. From the reaction mixture, we were able to isolate

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(11) The nonformation of *tert*-butyl-α-cumyl peroxide in the experiment described by Kharasch, Pauson, and Nudenberg,[4] is attributed to comparatively large quantities of the cobalt naphthenate used. When this, or cobalt-2-ethylhexoate is used as a reagent, it is important that small amounts of a dilute solution of the cobalt salt be added gradually over a 2- to 4-hr. period to obtain satisfactory yields. This procedure eliminates the evolution of oxygen which takes place in the presence of more concentrated solutions of cobalt salts.

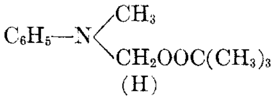
(12) Ng. Ph. Buu-Hoï, *Ann.*, **556**, 1 (1944).

(13) Robert Malec, Ph.D. thesis, University of Chicago, 1957.

(14) L. Horner and E. Schenk, *Ann.*, **566**, 69 (1950).

(15) W. H. Urry, O. O. Juveland, and F. W. Stacey, *J. Am. Chem. Soc.*, **74**, 6155 (1952).

N-methyl-*N*-*tert*-butylperoxymethylaniline (H) in yields in excess of 90%.



$$C_6H_5—N\begin{cases}CH_3\\ CH_2OOC(CH_3)_3\end{cases} \qquad (7)$$

(H)

Similar to other compounds containing a *tert*-butylperoxy group, the infrared spectrum of Compound H has bands at 1370 cm.$^{-1}$ (strong) and 1390 cm.$^{-1}$ (medium) indicating the presence of *tert*-butoxy groups. Below 880 cm.$^{-1}$ the spectrum is almost identical with that of dimethylaniline (no nuclear substitution).

Unlike the other peroxides we have described, compound H can be titrated iodometrically in acetic acid. It is soluble in hydrochloric acid. It is astonishingly stable. Its titer dropped only 5% after 24 hr. refluxing in benzene. With prolonged treatment with acids, it can be hydrolyzed to monomethylaniline.

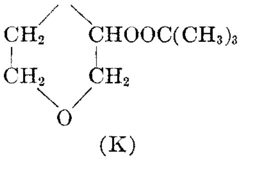
Reaction of p-xylene with tert-butyl hydroperoxide in the presence of cuprous salts. *p*-Xylene is expected to be more susceptible to free radical substitution reactions than cumene, which yields a weak radical. This shall be discussed in detail in a future publication. However, the expected peroxide was of interest to us as the preparation of a hydroperoxide from *p*-xylene is known to give very low yields.[16] The *p*-methylbenzyl *tert*-butyl peroxide (J) was prepared in the usual manner with 85% yield.

$$p\text{-}CH_3C_6H_4CH_2OOC(CH_3)_3 \qquad (8)$$

(I)

The infrared spectrum indicated the presence of all the bands characteristic for a *tert*-butoxy group.

Reaction of dioxane 1,4 with tert-butyl hydroperoxide in the presence of cuprous salts. The previous reactons indicated that in these substitution reactions, the peroxy group can substitute slightly activated primary, secondary, and tertiary hydrogens; that the activating group can be an aromatic ring, a double bond, a keto group, or a nitrogen atom. We prepared the peroxide of dioxane to show that an oxygen atom can also act as an activating group. We also wished to prepare a peroxide which is somewhat water soluble. Compound K, 2-*tert*-butylperoxy dioxane 1,4 was prepared in the usual manner and purified by chromatography. The yield was 50%.



(9)

(K)

After 1 week at 0°, the infrared spectrum indicated no decomposition. Preliminary tests indicated that peroxide K can be decomposed by heat without exploding.

Decomposition of tert-butyl hydroperoxide in iso-octane in the presence of cuprous chloride. Although a solution of *tert*-butyl hydroperoxide in iso-octane is stable when heated to 67°, the addition of 1 mole % of cuprous chloride to the hydroperoxide caused decomposition in approximately 20 min. The reaction is:

$$2(CH_3)_3COOH \xrightarrow[Cu_2Cl_2]{\text{iso-octane}} O_2 + 2(CH_3)_3COH + H_2O \qquad (10)$$

DISCUSSION

First let us discuss the decomposition of *tert*-hydroperoxides into oxygen and alcohols using metal salts, which act as both oxidants and reductants. The following chain mechanism has been suggested.[17]

$$ROOH + M^+ \longrightarrow RO^\cdot + M^{++} + (OH)^- \qquad (11)$$

$$ROOH + M^{++} \longrightarrow ROO^\cdot + M^+ + H^+ \qquad (12)$$

$$RO^\cdot + M^+ \longrightarrow RO^- + M^{++} \qquad (13)$$

$$RO^\cdot + ROOH \longrightarrow \text{Induced decomposition of peroxide (Ketone + Alcohol + }RO^\cdot) \qquad (14)$$

$$ROO^\cdot + M^{++} \longrightarrow R^+ + M^+ + O_2 \qquad (15)$$

The intermediate formation of a carbonium ion (Equation 15) could not be substantiated. Carbonium ions react with hydroperoxides to give peroxides (10), and if the reaction is carried out in acetic acid, as a solvent, they should form acetates. Increasing the concentration of the hydroperoxides leads however, to less and not more peroxide formation. Similarly, in acetic acid as a solvent, only traces of acetate are formed.

The oxygen evolution has to derive either from the interaction of 2 peroxy radicals (Equation 16) or from the reaction of a peroxy radical with a hydroperoxide (Equation 17).

$$2\ ROO^\cdot \longrightarrow 2\ RO^\cdot + O_2 \qquad (16)$$

$$ROO^\cdot + ROOH \longrightarrow ROH + O_2 + RO' \qquad (17)$$

At a higher hydroperoxide concentration, products start to appear, which obviously derive from the RO. radical. A definite proof has to come from studies with O^{18}.

Direct evidence of the existence of RO· radicals (Equation 11) has been obtained by running this reaction in water at 0°, in the presence of butadiene and using a large amount of ferrous salts.[18] The RO· radicals are picked up by the butadiene, and the radical formed dimerizes:

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[16] H. Hock and S. Lang, *Ber.*, **76**, 169 (1943).

[17] M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, **17**, 207, (1952). The present authors never observed the formation of symmetrical peroxides from hydroperoxides, in inert solvent, where acid catalyzed reaction could be excluded.

[18] M. S. Kharasch, F. S. Arimoto, and W. Nudenberg, *J. Org. Chem.*, **16**, 1556, 1951).

$$\mathrm{RO^{\cdot} + H_2C{=}CHCH{=}CH_2 \longrightarrow (ROC_4H_6)^{\cdot}} \quad (18)$$

$$\mathrm{2\,(ROC_4H_6)^{\cdot} \longrightarrow (ROCH_2CH{=}CHCH_2{-})_2} \quad (19)$$

The existence of ROO˙ radicals (Equation 12), as intermediates, was proven by a similar method.[5] Using excess butadiene as a solvent, and cobaltous salts as catalyst, the ROO˙ radicals are picked up by the butadiene. The resulting radical reacts with another hydroperoxide and a one-electron oxidizing agent to give dialkylperoxy butene:

$$\mathrm{ROO^{\cdot} + H_2C{=}CHCH{=}CH_2 \longrightarrow (ROOC_5H_6)^{\cdot}} \quad (20)$$

$$\mathrm{(ROOC_4H_6)^{\cdot} + ROOH + Ox \longrightarrow ROOC_4H_6OOR + H^+ + (Ox + e)} \quad (21)$$

Now let us consider the decomposition of hydroperoxides, which leads to the formation of peroxides. The apparent ability of a carbon free radical to react with a hydroperoxide and a 1-electron oxidizing agent simultaneously was demonstrated by isolating *tert*-butyl-α-cumyl peroxide, in good yields, when acetylperoxide was decomposed in cumene, in the presence of *tert*-butyl hydroperoxide.[10] This study suggested the following mechanism for this reaction:

$$\mathrm{(CH_3CO_2)_2 \longrightarrow 2\,CH_3^{\cdot} + 2\,CO_2} \quad (22)$$

$$\mathrm{CH_3^{\cdot} + C_6H_5(CH_3)_2CH \longrightarrow CH_4 + C_6H_5(CH_3)_2C^{\cdot}} \quad (23)$$

$$\mathrm{C_6H_5(CH_3)_2C^{\cdot} + ROOH \longrightarrow ROOH{\cdot}C(CH_3)_2C_6H_5} \quad \text{(Radical complex L)} \quad (24)$$

$$\mathrm{L + Ox \longrightarrow ROOC(CH_3)_2C_6H_5 + (Ox + e)} \quad (25)$$

Equation 24 proposes that free radicals can form a radical complex with a hydroperoxide, identical with a radical complex formed from a peroxy radical and a hydrocarbon. Later, Swarz and Smid[19] postulated a radical complex as intermediate, to explain the ability of benzoyloxy radicals, but not of methyl radicals, to abstract a hydrogen from trifluoro acetic acid. Hammond *et al.*[20] were forced to assume that some inhibitors can form loose complexes with radicals. An alternate possibility is that the reaction mixture contains a large concentration of comparatively stable ROO˙ radicals, and that this comparatively stable radical is capable of picking up all carbon radicals, as they are formed.

The comparatively fast decomposition of *tert*-butyl hydroperoxide in iso-octane indicates that the free radicals initially formed from the hydroperoxide are stabilized in a solvent containing reactive hydrogens. This favors the theory of a radical complex formation. The hydroperoxide is also more stable in aromatic solvents, which are known to stabilize radicals through complex formation.[21]

In subsequent papers, we shall show that radicals can react with benzoic and acetic acids, in the presence of 1-electron oxidizing agents, to give benzoates and acetates. The assumption of a comparatively stable acetoxy radical is incongruent with the known readiness of acetoxy radicals to break down into methyl radicals and carbon dioxide.

We established that metal salts generate both alkoxy (RO˙) and alkylperoxy (ROO˙) radicals from hydroperoxides; Further, that carbon free radicals are capable of reacting with hydroperoxides and a 1-electron oxidizing agent to form peroxides. The following mechanism is suggested for the metal salt catalyzed formation of a peroxide from an organic molecule, containing a slightly activated hydrogen a hydroperoxide.

$$\mathrm{ROOH + M^+ \longrightarrow RO^{\cdot} + M^{++} + OH^-} \quad (\text{M is Cu, Mn, or Co}^+) \quad (26)$$

$$\mathrm{RO^{\cdot} + R'H \longrightarrow ROH + R'^{\cdot}} \quad (27)$$

$$\mathrm{R'^{\cdot} + ROOH \longrightarrow R'{\cdot}HOOR} \quad (28)$$

$$\mathrm{ROOH + M^{++} \longrightarrow ROO^{\cdot} + M^+ + H^+} \quad (29)$$

$$\mathrm{ROO' + R'H \longrightarrow R'{\cdot}HOOR} \quad (30)$$

$$\mathrm{R'{\cdot}HOOR + Ox \longrightarrow R'OOR + (Ox + e) + H^+} \quad (31)$$

(The oxidant can be either $\mathrm{Me^{++}}$ or a hydroperoxide.)

The reaction between *tert*-butyl hydroperoxide and octene-1 gave both 1-*tert*-butylperoxyoctene-2, and 3 *tert*-butylperoxyoctene-1. An alternate mechanism for the formation of peroxides from an olefin, where the initial step is the addition of a peroxyradical to the double bond, must be rejected. (*cf.* 5c).

Another alternate mechanism to avoid the necessity of having to postulate a radical complex would be:

$$\mathrm{R'^{\cdot} + Ox \longrightarrow R'^{+} + (Ox + e)} \quad (32)$$

$$\mathrm{R'^{+} + ROOH \longrightarrow R'OOR + H^+} \quad (33)$$

This mechanism would predict that if the reaction is carried out in the presence of an excess of acetic acid, an appreciable amount of acetate should be formed. However, when *tert*-butyl hydroperoxide was decomposed by metal salts, in the presence of cumene in acetic acid as solvent, α-cumyl *tert*-butyl peroxide was still isolated in 92% yield. Therefore, reactions 32 and 33 do not occur. In subsequent papers, it will be shown that the acetates can be prepared by homolytic mechanism, but that they form only if the acetic acid present in the formation is kept to a low concentration. This is a requirement, which we will show, favors the homolytic mechanism.

The reactions described in this study do occur, to some extent, in the absence of metal salts. After 24 hr. heating of *tert*-butyl hydroperoxide in cumene at 105°, followed by distillation and chromatography, about 5% α-cumyl-*tert*-butyl peroxide could be isolated. This prompted us to present a mechanism where the only role of the metal salts is to initiate free radical reactions. However, the observation that with copper salts fewer by-products

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[19] M. Swarz and I. Smid, *J. Chem. Phys.*, **27**, 421 (1957).

[20] G. S. Hammond, E. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**,3238 (1955).

[21] G. A. Russel, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

are formed indicates that the metal salts do participate to some extent in these reactions. Their role is to stabilize the intermediate radical complexes. The evidence for this view will be presented in subsequent publications.

EXPERIMENTAL

The reactions we have described were carried out in an atmosphere of nitrogen gas. All of the reagents, with the exception of α-cumyl hydroperoxides were distilled prior to use. The purity of the hydroperoxides used is indicated in the individual experiments. The metal salts used were the ordinary laboratory reagent and unless indicated, were not finely powdered. The rate of the decomposition of the reaction mixture of the hydroperoxides was followed by titration at periodic intervals. The spinning band columns used were of the Piros-Glover type.

Preparation of compound B (α-cumylperoxycyclohexene). A mixture containing cyclohexene (0.9 mole), α-cumyl hydroperoxide (0.11 mole containing 75% of hydroperoxide), and cuprous chloride (0.1 g.) was heated at 70° for 20 hr. At the end of that time, a titration showed that 75% of the hydroperoxide had decomposed. The copper salt was collected on a filter. The volatile materials were removed at a pressure of 16 mm. The unreacted hydroperoxide was removed at 75°/0.1 mm. The residue (9 g.) was distilled at reduced pressure (98°/0.1 mm., n_{D}^{20} 1.5238). The yield of peroxide B was 90% on the basis of the hydroperoxide used.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; mol. wt. 232. Found: C, 77.8; H, 8.8; mol. wt. 220.

The infrared spectrum and the amount of unsaturation were in agreement with the proposed structure.

Preparation of compounds C and D. (C) $C_5H_{11}CH{=}CHCH_2OOC(CH_3)_3$; (D) $C_5H_{11}CHCH{=}CH_2OOC(CH_3)_3$.

(*a*) A mixture of octene-1 (0.35 mole), *tert*-butyl hydroperoxide (0.09 mole: 10 g. of 80% material), and cuprous chloride (0.1 g.) was heated to and maintained at 70° for 7 hr. At the end of that time, a titration showed that 80% of the hydroperoxide had been consumed. The copper salt was collected on a filter, while the low boiling materials in the filtrate were removed at 16-mm. pressure. The residue (7.6 g.) was distilled at reduced pressure. The material boiling at 37–42°/0.1 mm. was collected (6 g.: n_{D}^{20} 1.4290). This material was a mixture of compounds C and D. The yield, on the basis of the hydroperoxide consumed in the reaction was 85%. The infrared spectrum of this mixture indicated that it contained a small amount, less than 5% of an α,β unsaturated aldehyde (octenal).

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08; mol. wt. 200. Found: C, 72.3; H, 12.2; mol. wt. 190.

The material that boiled at 37–42°/0.1 mm. was carefully fractionated, using a spinning band column. We removed 10% of the total mixture, boiling at 42–56°/2.5 mm. It consisted of octenal and some of compound D. Two main fractions were obtained:

Fraction 1. 2.5 g. Compound D, b.p. 57°/2.5 mm.; n_{D}^{20} 1.4243.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.0; H, 12.2.

Fraction 2. 2.6 g. Compound C, b.p. 72°/2.5 mm.; n_{D}^{20} 1.4320.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.0; H, 11.9.

(*b*) The reaction described in (*a*) was repeated. In place of cuprous chloride, a 0.5% solution of cobalt 2-ethylhexoate in octene-1 (0.2 mole %) was added dropwise, over a period of 3 hr. At the end of that time, approximately 80% of the hydroperoxide had been consumed. A small amount of alumina was added and the solid collected on a filter. The filtrate was worked up in the same manner as described in section (*a*). The yield and the physical constants of compounds C and D were the same as described in section (*a*).

Preparation of compound E (tert-butyl-α-cumyl peroxide). (*a*) A mixture containing cumene (0.62 mole), *tert*-butyl hydroperoxide (0.29 mole containing 80% of a hydroperoxide), and cuprous chloride (0.2 g.) was heated at 67° for 18 hr. At the end of that time, a titration showed that 80% of the hydroperoxide had decomposed. The copper salt was collected on a filter. The volatile materials were removed at a pressure of 12 mm. A residue (24 g.) contained approximately 80–85% of compound E and approximately 15% of a mixture of acetophenone and dimethylphenylcarbinol (cumyl alcohol). The mixture was separated by distillation through a fractionating column. The pure peroxide E (60%) distilled at 60°/2 mm., n_{D}^{20} 1.4800.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 74.95; H, 9.7. Found: C, 74.80; H, 10.0.

The infrared spectrum of the compound E obtained in this manner was identical with the spectrum of *tert*-butyl-α-cumyl-peroxide prepared from dimethylphenylcarbinol and *tert*-butyl hydroperoxide.[9]

(*b*) The experiment just described was repeated. In place of cuprous chloride, a solution (0.5%) of cobalt 2-ethyl hexoate in cumene (0.2 mole %) was added dropwise during a period of 3 hr. At the end of that time, approximately 80% of the hydroperoxide had been consumed. A small amount of alumina was added, the mixture was shaken, and the solid collected on a filter. The low boiling materials were removed from the filtrate by distillation. An attempt to separate the residue by distillation through a spinning band was unsuccessful. This was attributed to the presence of considerable quantities of dimethylphenylcarbinol, which boiled at approximately the same temperature as the unsymmetrical peroxide. The pure peroxide E (n_{D}^{20} 1.4790) was obtained by chromatographic separation on alumina, using petroleum ether as the eluent. The yield of the unsymmetrical peroxide was 60%. The yield of the dimethylphenylcarbinol was approximately 30%.

A much higher yield (90%) of *tert*-butyl-α-cumyl peroxide was obtained when this same reaction was carried out at 100–110°. At that temperature, only a minute amount (0.05 mole %) of cobalt 2-ethyl hexoate was added. The reaction was usually complete in 30 min.

(*c*) A mixture containing cumene (0.4 mole), acetic acid (0.84 mole), *tert*-butyl hydroperoxide (0.14 mole, containing 85% of hydroperoxide), and manganous bromide (0.0006 mole; 4 mole % on the basis of the hydroperoxide used) was heated at 80° for 11 hr. At the end of that time, titration showed that 86% of the hydroperoxide had decomposed. The reaction mixture was poured into water and the layers separated. The organic layer was dried and distilled. The material which boiled at 50°/20 mm. was collected. Almost all of the residue distilled at 45°/0.15 mm. Ninety-two per cent of this material (n_{D}^{20} 1.4820) was *tert*-butyl-α-cumyl peroxide containing a minute amount of acetophenone (n_{D}^{20} 1.5338). The index of refraction of the pure *tert*-butyl-α-cumyl peroxide is n_{D}^{20} 1.4790–1.4800. A very satisfactory yield of *tert*-butyl-α-cumyl peroxide was obtained when cuprous salt was substituted for the manganese salt in the experiment just described.

Preparation of compound F (2-methyl-2-tert-butylperoxycyclohexanone). A mixture consisting of 2-methylcyclohexanone (0.52 mole), *tert*-butyl hydroperoxide (0.19 mole containing 80% hydroperoxide), and cuprous chloride (0.1 g.) was heated at 60° for 7 hr. At the end of that time, a titration indicated that 75% of the hydroperoxide had reacted. The copper salt was collected on a filter. The low boiling materials were removed from the filtrate by distillation at 12 mm. The residue (13.5 g.) was practically pure peroxide F (95%). Distillation of this material through a column (b.p. 66°/2 mm.; n_{D}^{20} 1.4431) gave the pure peroxide F in over 90% yield.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07; mol. wt. 200. Found: C, 65.9; H, 9.9; mol. wt. 189.

Preparation of compound G (2-tert-butylperoxycyclohexanone). A mixture consisting of cyclohexanone (0.61

mole), *tert*-butyl hydroperoxide (0.2 mole containing 90% of hydroperoxide), and cuprous chloride (0.1 g.) was heated at 92° for 8 hr. At the end of that time, a titration showed that 90% of the hydroperoxide had decomposed. The copper salt was collected on a filter. The volatile material was removed from the filtrate at a pressure of 12 mm. The residue, 12 g., was dissolved in hot benzene. Cooling produced a solid (3 g.) which was separated and collected on a filter. The solid material melted at 151–152° and did not depress the melting point of an authentic sample of adipic acid. The benzene was removed from the filtrate and the residue subjected to distillation. A fraction (4 g.) boiling at 52°/0.15 mm. was collected, leaving a residue I (5 g.). The distillate still contained a small amount of an acidic impurity. To remove it, the distillate was dissolved in benzene, and then washed with a water solution of sodium carbonate. The benzene was then removed at reduced pressure leaving an oil (n_D^{20} 1.4500) which was assumed to be compound G.

Preparation of compound H (N-methyl-N tert-butylperoxymethylaniline). A mixture containing dimethylaniline (0.19 mole), *tert*-butyl hydroperoxide (0.39 mole), cuprous chloride (0.0003 mole), and benzene (1.6 mole) was maintained at 35° for 12 hr. At the end of that time, iodometric titration indicated the loss of 50% of the active oxygen. Some neutral alumina was added, and filtered. The benzene and *tert*-butyl alcohol formed were distilled off *in vacuo*. The crude peroxide was purified by chromatographic separation through a short column of neutral alumina, using petroleum ether as the eluent. Small amounts of amine oxides were formed as by-products. The purified peroxide, b.p. 75°/0.1 mm., n_D^{20} 1.5160, was obtained in over 90% yield. It can be titrated iodometrically in acetic acid. It is soluble in dilute aqueous hydrochloric acid and its titer dropped only 5% after refluxing for 24 hr. in benzene.

Anal. Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.70; mol. wt. 209. Found: C, 69.1; H, 8.9; N, 7.0; mol. wt. 212.

Comparison of its infrared spectrum to that of dimethylaniline indicated no additional substitution in the aromatic ring. After prolonged warming in aqueous hydrochloric acid, monomethylaniline was isolated.

Preparation of compound J (p-methylbenzyl tert-butyl peroxide). A mixture consisting of *p*-xylene (1.0 mole), *tert*-butyl hydroperoxide (0.26 mole), and cuprous chloride (0.1 gram) was heated to 50° and maintained at that temperature for 10 hr. At the end of that time, titration showed that 50% of the hydroperoxide had been consumed. The lower boiling materials were removed *in vacuo*. The crude peroxide was purified by a chromatographic separation, through a short column of neutral alumina, using petroleum ether as an eluent. The yield was 0.55 mole (85%) on the basis of the hydroperoxide that was decomposed. The by-product was *p*-methylbenzaldehyde. The peroxide J is a pleasant smelling liquid, b.p. 65°/0.2 mm., n_D^{20} 1.4858.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; mol. wt. 194. Found: C, 74.40; H, 9.17; mol. wt. 186.

The infrared spectrum of the peroxide J had bands at 1360 cm.$^{-1}$ (strong) and 1385 cm.$^{-1}$ (medium), which indicated the presence of a *tert*-butyl group. The bands at 1190 cm.$^{-1}$ and 875 cm.$^{-1}$ are ascribed to the presence of the *tert*-butoxy group.

Preparation of compound K (tert-butylperoxydioxane 1,4). A mixture containing *tert*-butyl hydroperoxide (0.22 mole), dioxane 1,4 (1.00 mole), and cuprous chloride (0.05 g.) was heated to 70° and maintained at that temperature for 12 hr. At the end of that time, titration showed that 85% of the hydroperoxide had been consumed. The lower boiling materials were removed *in vacuo*. The infrared spectrum of the crude reaction product indicated strong keto and hydroxy bands. The peroxide was purified by chromatographic separation through a short neutral alumina column, using petroleum ether as an eluent. Yield of the peroxide K was 0.095 mole (50% on the basis of the hydroperoxide consumed).

The *tert*-butyl peroxy dioxane 1,4, b.p. 55°/0.25 mm., n_D^{20} 1.4325 is somewhat soluble in water. Its infrared spectrum contains bands at 1360 cm.$^{-1}$ (strong) and 1390 cm.$^{-1}$ (medium) indicating the presence of a *tert*-butyl group. The bands at 1185 cm.$^{-1}$ and 875 cm.$^{-1}$ are given to the presence of the *tert*-butoxy group.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15; mol. wt. 176. Found: C, 54.32; H, 8.93; mol. wt. 176.

Decomposition of tert-butyl hydroperoxide in iso-octane. A mixture containing *tert*-butyl hydroperoxide (0.1 mole), iso-octane (0.4 mole), and cuprous chloride (1 g.) was heated to 67°. A violent reaction followed. Within 20 min., all of the hydroxyperoxide decomposed and oxygen gas (0.5 mole) had evolved. The react on mixture did not react with dinitrophenyl hydrazine (no ketones), nor with concentrated HI (no peroxides).

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Kinetics and Mechanism of the Perkin Reaction

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The condensation of benzaldehyde with acetic anhydride to yield cinnamic acid, using various basic catalysts such as triethyl-, tripropyl-, tributyl-, and triisobutylamine, has been studied kinetically at 125–155° in kerosine as solvent. The rate of the formation of cinnamic acid as well as that of the disappearance of benzaldehyde has been followed by ultraviolet spectrophotometry. The rate was found to be expressed as k(benzaldehyde) (acetic anhydride) in an excess of the catalyst, while as k(benzaldehyde) (catalyst) in an excess of acetic anhydride. The variation of the rates with changing catalysts was shown to be ascribed to the variation of both frequency factor and energy of activation. A precise fit to the Hammett equation was observed with substituted benzaldehydes, with a positive ρ value of 2.25 at 135°. A mechanism involving a rate-determining attack of a complex of acetic anhydride with trialkylamine [$Ac_2O.R_3N$] on the carbonyl carbon of benzaldehyde is presented and discussed.

Although the Perkin reaction has long been studied as a problem of organic chemistry,[1] only a few kinetic and mechanistic studies[2] have so far been reported. Buckles and Bremer[2b] followed the triethylamine-catalyzed reaction of benzaldehyde and phenylacetic acid by estimating a reactant (benz-

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(1) For the review see, J. R. Johnson, *Org. Reactions*, **I**, 248 (1942).