[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1]]

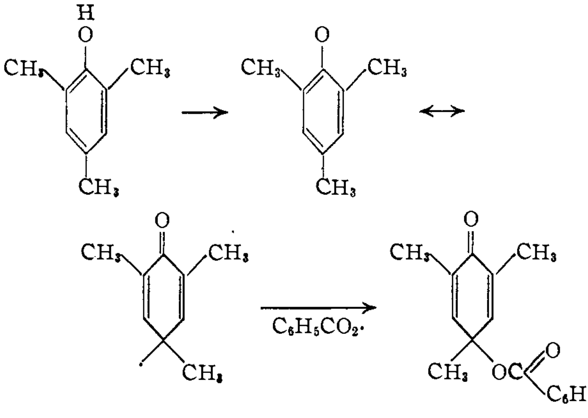
The Reaction of *t*-Butyl Hydroperoxide with Some Phenols

BY TOD W. CAMPBELL AND GALVIN M. COPPINGER

The phenolic antioxidant 2,6-di-*t*-butyl-*p*-cresol is converted by reaction with *t*-butyl hydroperoxide to 1-methyl-1-*t*-butylperoxy-3,5-di-*t*-butylcyclohexadiene-2,5-dione-4. This peroxide reacts with bromine in acetic acid to give in high yield 3,5-di-*t*-butyl-4-hydroxybenzaldehyde.

The efficiency of monohydric phenols as antioxidants varies widely with the type and position of substituents.[2-4] Thus phenol itself, which has essentially no activity, is converted to very potent antioxidants by substituting alkyl groups in the 2-, 4- and 6-positions. In view of this striking change in activity it is not unreasonable to suggest that the 2,4,6-trialkylphenols react with free radicals generated during an autoxidation process in a different manner than do the unsubstituted phenols.

The reaction of phenols with free radicals has been the subject of numerous papers, which it is not our purpose to review here. However, Cosgrove and Waters have made an interesting contribution in preliminary study of the mechanism whereby antioxidants react with free radicals.[5] They have decomposed benzoyl peroxide in the presence of various phenols, and then studied the products. Among other observations, they noted that mesitol, a very potent antioxidant, reacted to give the compound 4-benzoyloxy-2,4,6-trimethylcyclohexa-2,5-dienone.



Since, as has been well established, the process of autoxidation of olefins, fats and various hydrocarbons involves the intermediate formation of hydroperoxides by some scheme such as

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot$$
$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$RO_2\cdot + RH \longrightarrow R\cdot + ROOH$$

it was felt that it would be of interest to examine the reaction of various phenols with a substrate composed of *t*-butyl hydroperoxide, at a temperature at which the hydroperoxide is decomposing into free radicals by essentially the reverse of the above equations.[6] Consequently, a number of phenols were treated in such a manner. In most cases, the reaction, which was followed spectrophotometrically, was slow. Thus after 24 hours most of the phenols had been partially converted to resins. However, those phenols which were good antioxidants were rapidly (about 1 hour) and cleanly converted to new products with ultraviolet maxima at 234 mμ. In three of the four cases in which this change occurred, the products were very viscous liquids which could not be induced to crystallize. However, with 2,6-di-*t*-butyl-*p*-cresol a beautifully crystalline product was obtained. It was with this material that most of the work was done.

The product of the reaction of *t*-butyl hydroperoxide with di-*t*-butyl-*p*-cresol had the composition, $C_{19}H_{32}O_3$. It melted without decomposition at 74°; however, if the temperature of the melt was raised to the point at which small bubbles just began to form (125–150°) and the source of heat was removed, the evolution of gas continued with increasing vigor until the last stages were explosively violent. From the vapors of the spontaneously decomposing product were isolated copious amounts of acetone, as the 2,4-dinitrophenylhydrazone. The non-volatile residue was a viscous oil of complex nature, which was not characterized.

The ultraviolet and infrared spectra (Figs. 1 and 2) show no evidence of hydroxyl groups; however, the twin bands at about 6 μ, characteristic of a

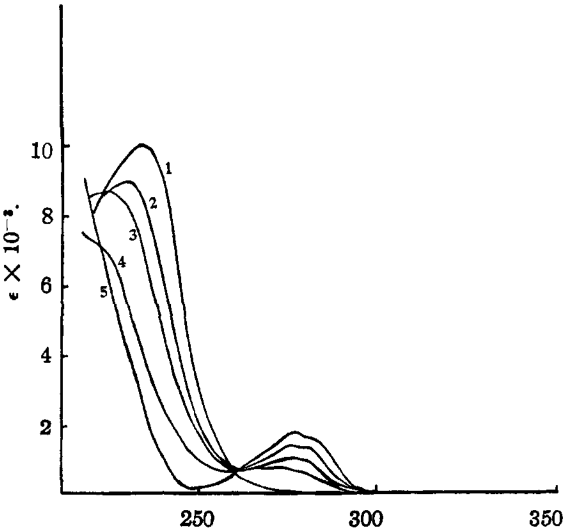


Fig. 1.—Conversion of 2,6-di-*t*-butyl-*p*-cresol to 2,6-di-*t*-butyl-4-*t*-butylperoxy-4-methylcyclohexa-2,5-dienone: time scale, decreasing maximum at 275 mμ, min.: 1, 0; 2, 15; 3, 30; 4, 45; 5, 60.

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] E. M. Bickoff, *J. Am. Oil Chem. Soc.*, **28**, 65 (1951).

[3] H. Morawetz, *Ind. Eng. Chem.*, **41**, 1442 (1949).

[4] R. H. Rosenwald, J. R. Hoatson and J. A. Chenicek, *ibid.*, **42**, 162 (1950).

[5] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 388 (1951).

[6] F. H. Seubold, Jr., F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 18 (1951).

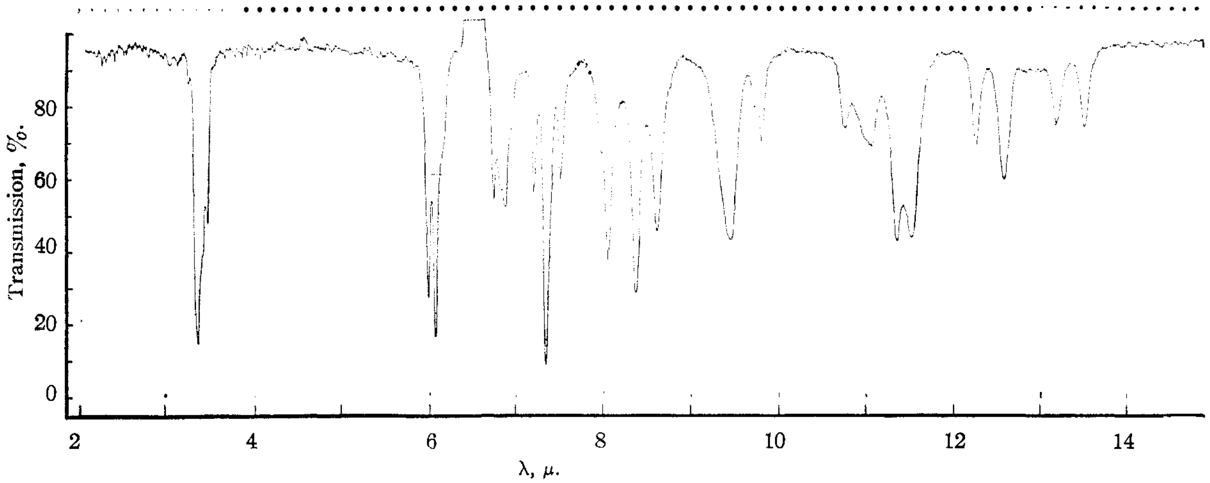
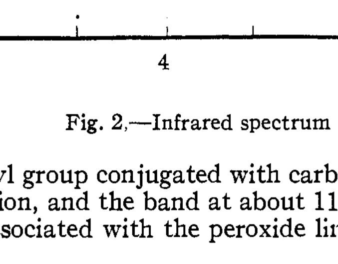


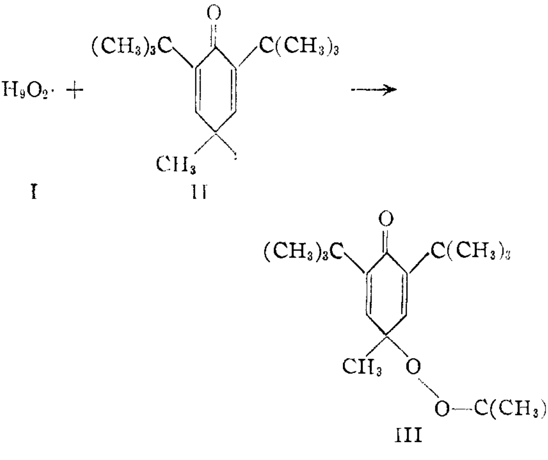
Fig. 2.—Infrared spectrum of 2,6-di-*t*-butyl-4-*t*-butylperoxy-4-methyl-cyclohexa-2,5-dienone.

carbonyl group conjugated with carbon–carbon unsaturation, and the band at about 11.4 μ which has been associated with the peroxide linkage,[7] are apparent.

The original product, $C_{19}H_{32}O_3$, reacted with bromine in acetic acid to give an excellent yield of 4-hydroxy-3,5-di-*t*-butylbenzaldehyde.



On the basis of the above observations, we propose that the product from 2,6-di-*t*-butyl-*p*-cresol is 1-methyl-1-*t*-butylperoxy-3,5-di-*t*-butylcyclohexadieneone-4 (III), derived by combination of radicals I and II.



The function of the phenol as an antioxidant can thus be considered to be twofold. First, it may prevent initiation of chain reactions by hydrogen atom exchange with a radical from the substrate, the resulting phenol

$$R\cdot + ArOH \longrightarrow ArO\cdot + RH$$

radical being sufficiently stabilized by resonance so that it is not capable of initiating a chain reaction. Secondly, the phenol radical is itself an antioxidant, since it may tie up by direct combination radicals which are capable of initiating a chain.

$$ArO\cdot + ROO\cdot \longrightarrow \text{peroxide}$$

It is especially noteworthy that this last reaction involves specifically the peroxy radicals, since the peroxides are produced in essentially quantitative yield, and no evidence was observed for the production of any similar product involving combination of the phenol with any other radicals present, although such may occur in a reversible manner.

Although the formation of an organic peroxide from a simple phenol is somewhat surprising, it is not inconsistent with results reported by Seubold Rust and Vaughan on the vapor phase decomposition of *t*-butyl hydroperoxide,[5] who showed that alkyl radicals combine readily with *t*-butyl peroxy radicals to give dialkyl peroxides.

$$R\cdot + R'O_2\cdot \longrightarrow ROOR'$$

The conversion of the peroxide III to 4-hydroxy-2,6-di-*t*-butylbenzaldehyde by the agency of bromine occurs by a mechanism which is at the moment not clear. It does, however, indicate that the molecular skeleton has not been altered during peroxide formation.

The 4-hydroxy-2,6-di-*t*-butylbenzaldehyde was also synthesized by the reaction of 2,6-di-*t*-butyl-*p*-cresol with bromine. Certain unusual aspects of this reaction as carried out in various solvents will be described in a future communication.

Experimental

Reaction of Phenols with *t*-Butyl Hydroperoxide.—One gram of the appropriate phenol was dissolved in 10 ml. of *t*-butanol and 5 ml. of *t*-butyl hydroperoxide was added, followed by two drops of a dilute solution of cobalt naphthenate in ethyl acetate. The solutions were heated for periods up to 24 hours. The phenols examined included: phenol, *p*-chlorophenol, *p*-phenylphenol, *p*-hydroxybenzaldehyde, *p*-*t*-butylphenol, *p*-cresol, 2-chloro-4-*t*-butylphenol, *p*-nitrophenol, 2-methoxy-4-methylphenol, 2,2-di-(*p*-hydroxyphenyl)-propane, mesitol, 6-*t*-butyl-2,4-dimethylphenol, 4,4'-dimethyl-6,6'-di-*t*-butyl-2,2'-methylenebisphenol and 2,6-di-*t*-butyl-*p*-cresol.

As the reaction progressed, the spectra of the reaction mixtures were measured from time to time; all but the last four compounds showed a gradual decrease in the phenol

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[7] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

maximum, with a concurrent darkening and resinification. The last four compounds reacted rapidly (1 hour) with the hydroperoxide, with complete disappearance of the phenol maximum, and appearance of a new maximum at about 235 mμ (Fig. 1). These products were isolated by evaporating volatiles on the steam-bath. The residues were viscous oils, except in the case of 2,6-di-*t*-butyl-*p*-cresol, which was beautifully crystalline. This product will be described in detail.

Product of the Reaction between Di-*t*-butyl-*p*-cresol and *t*-Butyl Hydroperoxide.—The crude crystalline material, obtained in quantitative yield, was recrystallized from isooctane. It crystallized as thick blunt needles, m.p. 74°. Its ultraviolet and infrared spectra (Figs. 1 and 2) indicate peroxide, conjugated carbonyl, but no hydroxyl.

Anal. Calcd. for $C_{19}H_{32}O_3$: C, 74.0; H, 10.5. Found: C, 73.7, 74.0; H, 10.5, 10.5.

Crystals of this compound on extended exposure to light and air gradually turn yellow. It is not affected by long boiling with zinc and acid in methanol. It is reduced to the starting phenol by lithium aluminum hydride.

Thermal Decomposition of the Peroxide.—About 300 mg. of the crystalline material melting at 74° was heated until bubbles began to form (about 125–150°). The heat was removed, and the reaction mixture continued to evolve gas more and more vigorously, until the reaction reached almost explosive violence. The gases evolved were trapped, and treated with 2,4-dinitrophenylhydrazine, thus yielding copious amounts of acetone 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 126°, the acetone having resulted from the thermal decomposition of a *t*-butoxy radical.

Reaction of the Peroxide with Bromine.—Ten grams of the peroxide was dissolved in 250 ml. of glacial acetic acid. Eight grams (1.5 moles) of bromine was added, and the mixture allowed to stand overnight. Next day the mixture was poured into water, and the crystalline solid isolated and recrystallized from alcohol. The product, 4-hydroxy-3,5-di-*t*-butylbenzaldehyde, melted at 189°, and was obtained in a yield of 82%.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.9; H, 9.47. Found: C, 76.7; H, 9.52.

It formed a 2,4-dinitrophenylhydrazone, melting at 235–236° uncor. Its absorption spectrum (Fig. 3) is characteristic of *p*-hydroxybenzaldehydes.[8]

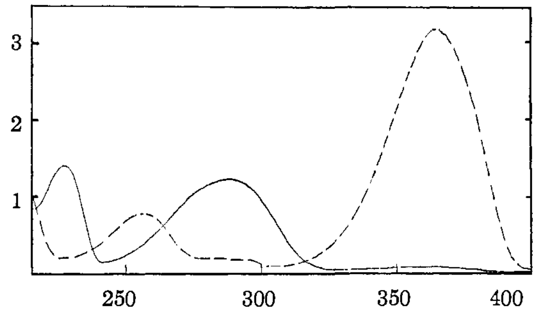

Fig. 3.—Spectrum of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde: —, neutral; - - -, basic.

Alternative Synthesis of 3,5-Di-*t*-butyl-4-hydroxybenzaldehyde.—One gram of 2,6-di-*t*-butyl-*p*-cresol in 50 ml. of *t*-butanol was treated with 1.4 g. of bromine at 30°. The temperature rose to about 50°; after one hour the crystalline product was filtered off, washed with thiosulfate solution, and recrystallized from methanol. The product melted at 189°, and was obtained in 85% yield.

Acknowledgments.—We wish to thank Glen F. Bailey and Stanley Friedlander for infrared spectral data, and Mrs. Mary Kilpatrick for ultimate analyses.

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[8] H. W. Lemon, This Journal, 69, 2998 (1947).

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[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

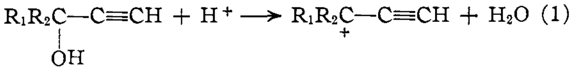
Organic Peroxides. XVI. Acetylene Peroxides and Hydroperoxides—A New Class of Organic Peroxides

By Nicholas A. Milas and Orville L. Mageli

The synthesis of a hitherto unknown class of organic peroxides, acetylene peroxides, is herein reported. Three types of this class of organic peroxides have been synthesized: (1) acetylene hydroperoxides comparable to acetylenecarbinols; (2) acetylene dihydroperoxides comparable to acetylene glycols; and (3) alkynyl peroxides comparable to alkynyl ethers. These peroxides are unusually stable and, in this respect, are comparable to saturated tertiary alkyl peroxides and hydroperoxides.

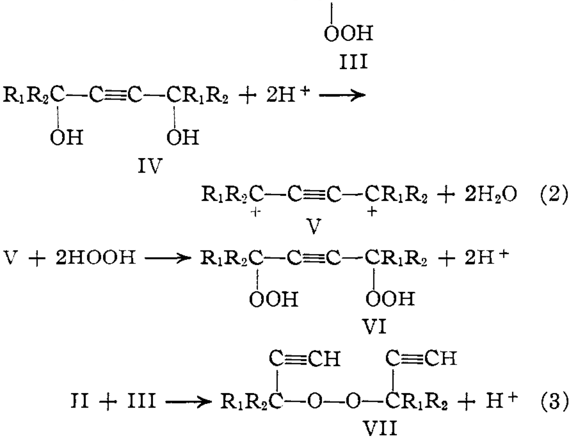
Acetylene peroxides or hydroperoxides analogous to acetylenic carbinols, glycols or ethers are not known. The purpose of the present communication is to describe the preparation and some of the properties of this new class of organic peroxides.

In general, these peroxides are prepared by a modification of the method originally published from this Laboratory.[1] It essentially consists in allowing an acetylenecarbinol (I) or glycol (IV) in which R_1 and R_2 are hydrocarbon radicals to react, at low temperatures, with hydrogen peroxide in the presence of a suitable strength of sulfuric acid. Three different types of acetylene peroxides have been prepared: (1) acetylene hydroperoxides (III),



$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{R_1R_2C}}\mathrm{{-}C{\equiv}CH} + \mathrm{H^+} \longrightarrow \underset{+}{\mathrm{R_1R_2C}}\mathrm{{-}C{\equiv}CH} + \mathrm{H_2O} \quad (1)$$

I II



$$\mathrm{II} + \mathrm{HOOH} \longrightarrow \underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{R_1R_2C}}\mathrm{{-}C{\equiv}CH} + \mathrm{H^+}$$

III

$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{R_1R_2C}}\mathrm{{-}C{\equiv}C{-}}\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CR_1R_2}} + 2\mathrm{H^+} \longrightarrow$$

IV

$$\underset{+}{\mathrm{R_1R_2C}}\mathrm{{-}C{\equiv}C{-}}\underset{+}{\mathrm{CR_1R_2}} + 2\mathrm{H_2O} \quad (2)$$

V

$$\mathrm{V} + 2\mathrm{HOOH} \longrightarrow \underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{R_1R_2C}}\mathrm{{-}C{\equiv}C{-}}\underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{CR_1R_2}} + 2\mathrm{H^+}$$

VI

$$\mathrm{II} + \mathrm{III} \longrightarrow \overset{\substack{\mathrm{C{\equiv}CH}\\ |}}{\mathrm{R_1R_2C}}\mathrm{{-}O{-}O{-}}\overset{\substack{\mathrm{C{\equiv}CH}\\ |}}{\mathrm{CR_1R_2}} + \mathrm{H^+} \quad (3)$$

VII

(2) acetylene dihydroperoxides (VI) and (3) dialkynyl peroxides (VII).

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[1] N. A. Milas, U. S. Patent 2,223,807, Dec. 3 (1940); N. A. Milas and D. M. Surgenor, This Journal, 68, 205 (1946).