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]

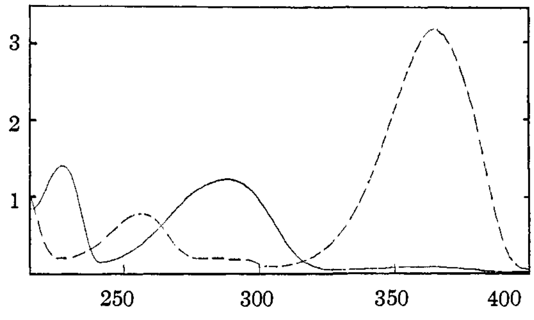


Fig. 3.—Spectrum of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde: —, neutral; - - -, basic.

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.

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

ALBANY 6, CALIFORNIA RECEIVED SEPTEMBER 4, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

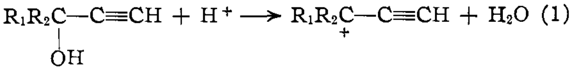
Organic Peroxides. XVI. Acetylene Peroxides and Hydroperoxides—A New Class of Organic Peroxides

BY NICHOLAS A. MILAS AND ORVILLE L. MAGELI

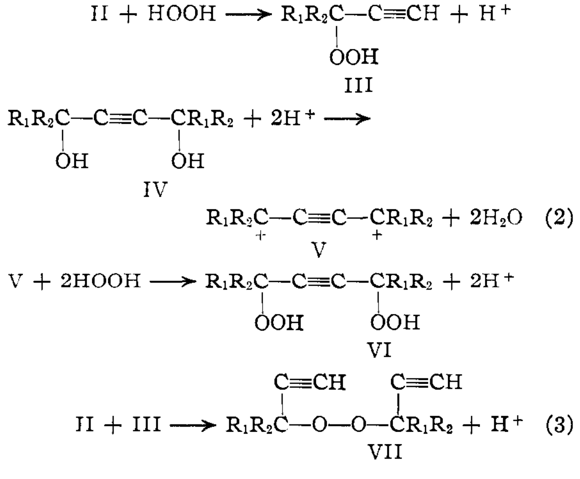
The synthesis of a hitherto unknown class of organic peroxides, acetylene peroxides, is herein reported. Three types of this class of organic peroxides have been synthesized: (1) acetylene hydroperoxides comparable to acetylenecarbinols; (2) acetylene dihydroperoxides comparable to acetylene glycols; 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),



$$\underset{\text{I}}{R_1R_2\underset{\mathrm{OH}}{\underset{|}{C}}—C{\equiv}CH} + H^+ \longrightarrow \underset{\text{II}}{R_1R_2\overset{}{\underset{+}{C}}—C{\equiv}CH} + H_2O \quad (1)$$



$$\text{II} + \text{HOOH} \longrightarrow \underset{\text{III}}{R_1R_2\underset{\mathrm{OOH}}{\underset{|}{C}}—C{\equiv}CH} + H^+$$

$$\underset{\text{IV}}{R_1R_2\underset{\mathrm{OH}}{\underset{|}{C}}—C{\equiv}C—\underset{\mathrm{OH}}{\underset{|}{C}}R_1R_2} + 2H^+ \longrightarrow \underset{\text{V}}{R_1R_2\underset{+}{C}—C{\equiv}C—\underset{+}{C}R_1R_2} + 2H_2O \quad (2)$$

$$\text{V} + 2\text{HOOH} \longrightarrow \underset{\text{VI}}{R_1R_2\underset{\mathrm{OOH}}{\underset{|}{C}}—C{\equiv}C—\underset{\mathrm{OOH}}{\underset{|}{C}}R_1R_2} + 2H^+$$

$$\text{II} + \text{III} \longrightarrow \underset{\text{VII}}{R_1R_2\overset{C\equiv CH}{\overset{|}{C}}—O—O—\overset{C\equiv CH}{\overset{|}{C}}R_1R_2} + H^+ \quad (3)$$

(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).

The peroxide (VII) is also formed as a by-product during the preparation of the hydroperoxide (III). Like tertiary alkyl hydroperoxides acetylene hydroperoxides can be easily alkylated with *t*-butyl alcohol to produce very stable *t*-butyl alkynyl peroxides. For example, 2,5-dimethyl-2,5-di-(*t*-butylperoxy)-hexyne-3 (VIII) was prepared in 88% yield from 2,5-dimethyl-2,5-dihydroperoxyhexyne-3 and *t*-butyl alcohol in the presence of sulfuric acid.

The formation of acetylene hydroperoxides in strong acid solutions was surprising in view of the fact that comparable alkenyl hydroperoxides cannot be prepared by this method. The instability of the latter in strong acid media is well known, and attempts to prepare α-cumyl hydroperoxide from either α,α-dimethylbenzyl alcohol or α-methylstyrene and hydrogen peroxide in the presence of these media led instead to a quantitative yield of phenol and acetone.[2]

Apparently in the formation of acetylene peroxides the intermediate carbonium ions (II) and (V) are strongly stabilized under our experimental conditions and in view of the high yields obtained the formation of the allenic carbonium ions[3] seems to be minimized.

The presence of the acetylene bond in acetylene hydroperoxides (III) and in dialkynyl peroxides (VII) was shown by infrared spectra and by the precipitation of insoluble silver salts in an ammoniacal alcoholic silver nitrate solution. In the case of the symmetrically substituted acetylene dihydroperoxides (VI) and (VIII) infrared spectra failed to show the presence of triple bonds. However, upon catalytic hydrogenation these peroxides absorbed the required amount of hydrogen and formed the expected saturated glycols.

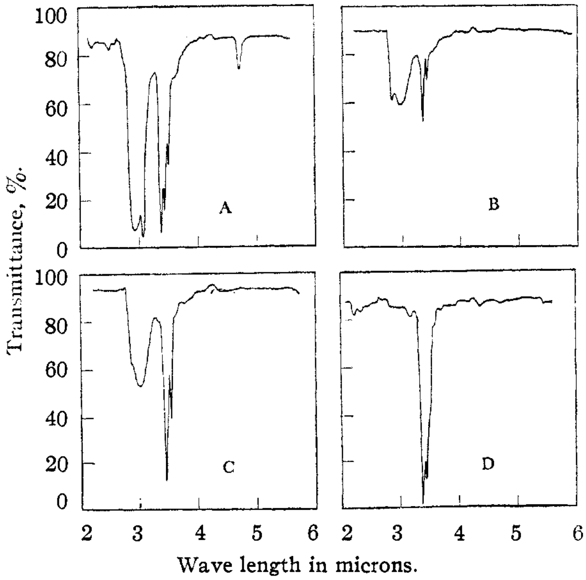

Fig. 1.—Infrared spectra of acetylene peroxides. Curve A, 3-methyl-3-hydroperoxypentyne-1; B, 2,5-dimethyl-2,5-dihydroperoxyhexyne-3, 5% in $CHCl_3$; C, 1,1′-dihydroperoxy-1,1′-dicyclohexylacetylene, 10% in $CHCl_3$; 2,5-dimethyl-2,5-di-(*t*-butylperoxy)-hexyne-3.

The thermal and acid-catalyzed decomposition of these peroxides is now being investigated and the results will be reported elsewhere.

Acknowledgment.—We are indebted to Lucidol Division of Novadel-Agene Corporation for financial support of this investigation and to Buffalo Electro-Chemical Co. for a generous supply of 50% hydrogen peroxide. For the combustion analyses and the infrared spectra we wish to thank Dr. Nagy and his associates of this Institute.

Experimental Part

3-Methyl-3-hydroperoxybutyne-1.—To a cold (−4°) mixture of hydrogen peroxide (35.4 g. of 50%) and sulfuric acid (55.7 g. of 95.5%) was added dropwise with rapid stirring 20 g. of 3-methylbutyn-1-ol-3, b.p. 100–104° (760 mm.)[4] in the course of 30 min. The temperature of the mixture was maintained at −4 to 0°. After five hours of stirring at 0° solid ammonium sulfate was added to moderate the reaction and to salt out the organic peroxide which was taken up in ether. The ethereal solution was shaken with a saturated solution of ammonium sulfate, dried over magnesium sulfate, filtered and the ether removed under reduced pressure; yield of the crude peroxide, 23.3 g. (98%). This, however, contained 73% of the hydroperoxide, the remainder being mainly dialkynyl peroxide. Purification was effected by fractionation under reduced pressure and the fraction boiling 42–42.2° (17 mm.) collected and analyzed; $n^{25}D$ 1.4295; $d^{25}{}_4$ 0.954; MR_D (calcd.),[5] 27.13; MR_D(obsd.), 27.07.

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.06; (O), 16.0. Found: C, 60.46; H, 8.06; (O), 14.6.

This hydroperoxide gives a copious precipitate with ammoniacal silver nitrate solution.

3-Methyl-3-hydroperoxypentyne-1.—To a cold mixture (0°) of 30.6 g. of 50% hydrogen peroxide and 48 g. of 95.5% sulfuric acid was added dropwise with rapid stirring 20 g. of 3-methyl-3-hydroxypentyne-1, b.p. 122–123° (761 mm.),[6] in the course of one-half hour. The temperature should not be allowed to rise above +5° during the initial stages of the reaction. Stirring was continued for 4.5 hours longer then the mixture diluted with an equal volume of saturated ammonium sulfate solution and extracted with ether. The ether extract was shaken with magnesium carbonate to remove traces of sulfuric acid, then dried over magnesium sulfate, filtered and the ether removed under reduced pressure; yield 22 g. (94%). This had a purity of 85% of hydroperoxide, the remainder was mainly dialkynyl peroxide. To purify it further it was fractionated under reduced pressure and the fraction boiling 38–40° (5 mm.) collected and analyzed; $n^{25}D$ 1.4369; $d^{25}{}_4$ 0.9547; MR_D (calcd.), 31.63; MR_D(obsd.), 31.32.

Anal. Calcd. for $C_6H_{20}O_2$: C, 63.13; H, 8.83; (O), 14.0. Found: C, 62.73; H, 8.85; (O), 13.4.

This hydroperoxide also gave a copious precipitate with ammoniacal alcoholic silver nitrate solution. The infrared spectrum of this hydroperoxide is shown in Fig. 1A.

2,5-Dimethyl-2,5-dihydroperoxyhexyne-3.—Following the same technique as that used under the previous preparation, 50 g. of 2,5-dimethyl-2,5-dihydroxyhexyne-3[7] (added in small portions in the course of one hour) was allowed to react with a mixture of 52.5 g. of 50% hydrogen peroxide and 69 g. of 95.5% sulfuric acid maintained at 0 ± 5°. The reaction was carried out in a tall 300-cc. open beaker. A yield of 52 g. (85%) of a solid product was obtained having a purity of 92%. This was recrystallized once from benzene; m.p. 107–109° (dec.).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10; (O), 18.4. Found: C, 55.45; H, 8.24; (O), 18.1.

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(2) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950); M. S. Kharasch and J. G. Burt, *ibid.*, **16**, 150 (1951).

(3) G. F. Hennion and D. E. Maloney, This Journal, **73**, 4735 (1951).

(4) J. F. Froning and G. F. Hennion, *ibid.*, **62**, 654 (1940).

(5) N. A. Milas, D. M. Surgenor and L. H. Perry, *ibid.*, **68**, 1617 (1946).

(6) "Beilstein," Vol. I, p. 235, 1928.

(7) A. Babayan, *Bull. Armenian Acad. Sci. U. S. S. R.* 1941, No. 5/6 (10/11) 121–45; *C. A.*, **40**, 3394 (1946).

In view of the symmetrical structure of this peroxide, the infrared spectrum (Fig. 1B) failed to show the presence of an acetylene bond. However, the peroxide absorbed 4.76 moles of hydrogen per mole when catalytically hydrogenated in glacial acetic acid using platinum oxide as catalyst, a value which is in close agreement with the theoretical of 4.00. The higher experimental value indicates some hydrogenolysis of the glycol formed. When 2 g. of the dihydroperoxide was hydrogenated in absolute alcohol, about 2 g. of a crude product was obtained; m.p. 77–78°. This was recrystallized from *n*-pentane into long, colorless needles; m.p. 88–89°. 2,5-Dimethylhexanediol-2,5 is reported to melt at 88.5–89°.[8]

1,1′-Dihydroperoxy-1,1′-dicyclohexylacetylene.—This dihydroperoxide was prepared in exactly the same manner as the previous dihydroperoxide. 1,1′-Dihydroxy-1,1′-dicyclohexylacetylene[9] (10 g.) was slowly added in small portions with rapid stirring to a cold (0°) mixture of hydrogen peroxide (9.6 g. of 50%) and sulfuric acid (14 g. of 95.5%). After five hours of stirring the product was recovered as before; yield 9 g. (79%). This titrated 85% as dihydroperoxide. It was recrystallized from cyclohexane, m.p. 95° (dec.).

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72; (O), 12.6. Found: C, 66.25; H, 8.87; (O) ,11.8.

The infrared spectrum of this dihydroperoxide is shown in Fig. 1C.

Di-(3-methylbutynyl)-3-peroxide.—To 12.7 g. of 70% cold (−3 to 0°) sulfuric acid was added dropwise with stirring a mixture of 6.05 g. of 3-methyl-3-hydroperoxybutyne-1 and 5.07 g. of 3-methyl-3-hydroxybutyne-1 in the course of one-half hour. Stirring was continued at 0 to +5° for 4.5 hours; then the mixture diluted with two volumes of water and extracted with *n*-pentane. The pentane solution was extracted twice with 10% sodium hydroxide solution, washed with water and dried. Finally, the pentane was removed and the residue distilled under reduced pressure and the portion boiling at 60° (76 mm.) collected and analyzed; yield of the pure product, 23%.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49. Found: C, 71.63; H, 8.61.

This peroxide is a very sweet smelling liquid and the presence of the acetylene groups was shown by a copious precipitate formed with ammoniacal alcoholic silver nitrate solution. Because of its reactivity with hydrogen iodide to form black solutions our present methods of analysis for peroxidic oxygen are not satisfactory for analysis of this peroxide as well as those that follow.

Di-(3-methylpentynyl)-3-peroxide.—This dialkynyl peroxide was prepared in exactly the same manner as its lower homolog. A yield of 34% of a sweet smelling liquid was obtained boiling at 53–55° (2 mm.); n^{25}_D 1.4390; d^{25}_4 0.903; MR_D(calcd.), 57.47; MR_D(obsd.), 56.65.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 70.83; H, 9.25.

This peroxide also gives a copious precipitate with ammoniacal alcoholic silver nitrate solution.

2,5-Dimethyl-2,5-di-(*t*-butylperoxy)-hexyne-3.—To a cold mixture (0°) of 6 g. of *t*-butyl alcohol and 11.2 g. of 70% sulfuric acid was slowly added with stirring 4.7 g. of 2,5-dimethyl-2,5-dihydroperoxyhexyne-3 in the course of 15 minutes. Stirring was continued at room temperature for five hours longer, then the mixture diluted with two volumes of water and extracted with ether; the ethereal solution dried and the ether removed under reduced pressure. A yield of 6.8 g. (88.3%) was obtained. This was distilled under reduced pressure and the fraction boiling at 65–67° (2 mm.) collected and analyzed; n^{25}_D 1.4219; d^{25}_4 0.881; MR_D (calcd.), 81.78; MR_D(obsd.), 82.61.

Anal. Calcd. for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found: C, 67.02; H, 10.71.

The infrared spectrum of this peroxide is shown in Fig. 1D.

CAMBRIDGE 39, MASS. RECEIVED OCTOBER 3, 1951

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[8] "Beilstein," Vol. I, p. 256, 1928.

[9] A. W. Johnson, "The Chemistry of the Acetylenic Compounds," Vol. 1, Edward Arnold and Co., London, 1946, p. 138.

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

The Dehydration of Methylalkylcyclopropylcarbinols. Isolation and Purification of 2-Cyclopropylalkenes[1]

BY VERNON A. SLABEY AND PAUL H. WISE

Ten 2-cyclopropyl-1- and -2-alkenes have been prepared from methyl cyclopropyl ketone by condensing the ketone with various Grignard reagents and dehydrating the resultant methylalkylcyclopropylcarbinols. Both alumina at 200 to 250° and sulfuric acid were found to be satisfactory dehydrating agents. Isolation of both the position and geometrical 2-cyclopropylalkene isomers in high purity was accomplished by fractional and azeotropic distillations. Melting points, boiling points, refractive indices, densities and heats of combustion are reported for the ten cyclopropylolefins. Methyl, ethyl, propyl and butyl cyclopropyl ketones were isolated as ozonolysis fragments of the cyclopropylolefins, and the melting points of their 2,4-dinitrophenylhydrazones are given.

The preparation and purification of a series of cyclopropylalkenes was undertaken in order to provide pure hydrocarbon samples for an investigation of the effect of molecular structure on physical and chemical properties. The reaction of various Grignard reagents with methyl cyclopropyl ketone[2] and dehydration of the resultant methylalkylcyclopropylcarbinols offered a possible method of synthesizing the cyclopropylalkenes. The previous work of Bruylants[3] and Henry[4] showed that Grignard reactions of the type proposed were suitable for preparing the methylalkylcyclopropylcarbinols. The practicability of the dehydration of cyclopropylcarbinols as a synthetic method, however, had not been established when this research was begun, although dehydrations of dimethyl[5–8] and methylethylcyclopropylcarbinol[5,9] with sulfuric acid,[5] oxalic acid[6] or acetic anhydride[7–9] were reported. In an investigation which occurred concurrently with the present work, Van Volkenburgh, *et al.*,[10] found that of three catalytic methods for dehydrating dimethylcyclopropylcarbinol, the

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[1] Presented before the Organic Division of the American Chemical Society, Chicago, Ill., September 3–8, 1950.

[2] Commercially available from U. S. Industrial Chemicals Inc., 60 E. 42nd Street, New York, N. Y., at the time this research was begun.

[3] P. Bruylants, *Bull. soc. chim. Belg.*, **36**, 153 (1927).

[4] J. Henry, *ibid.*, **40**, 647 (1931).

[5] N. van Keersbilck, *ibid.*, **38**, 208 (1929).

[6] N. Zelinsky, *Ber.*, **40**, 4743 (1907).

[7] N. Kizhner and V. Klavikordov, *J. Russ. Phys. Chem. Soc.*, **43**, 597 (1910).

[8] D. Alexejew, *ibid.*, **37**, 419 (1905).

[9] P. Bruylants, *Rec. trav. chim.*, **28**, 224 (1908).

[10] R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 172 (1949).