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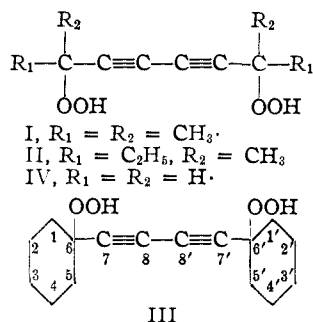
Organic Peroxides. XVIII. Diacetylenic Dihydroperoxides<sup>1</sup>

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Organic peroxides which contain two acetylenic groups in conjugation and two hydroperoxy groups in the same molecule have not been previously described. Four of these peroxides have now been synthesized and some of their properties as well as their infrared spectra are herein reported.

In a previous publication<sup>2</sup> we reported the synthesis of some organic peroxides containing isolated acetylenic bonds and hydroperoxy groups in the same molecule. We now wish to report the synthesis of some organic peroxides which contain two acetylenic bonds in conjugation and two hydroperoxy groups in the same molecule. Examples of this group of organic peroxides are shown by structures I, II, III, IV.



corresponding diacetylenic glycols by the general method previously reported from this Laboratory.<sup>3</sup> In certain cases, however, pure peroxides were obtained only by carrying out the reaction in a two-phase system.<sup>4</sup> Table I lists some of these peroxides together with some of their properties and analytical data.

The structure of these peroxides was established by quantitative hydrogenation and infrared spectra. Infrared spectra fail to show the presence of triple bonds in symmetrically substituted monoacetylenic compounds.<sup>2</sup> However, in diacetylenic compounds each triple bond is unsymmetrically substituted and shows a weak band at 4.6 μ.<sup>5</sup> Monohydroperoxides show a strong band at 11.9 μ which is characteristic of the hydroperoxy group.<sup>6,7</sup> A definite comparison between the diacetylenic dihydroperoxides and the corresponding diacetylenic glycols can be made by examining their infrared spectra. A typical example of these spectra is shown in Figs. 1 and 2.

TABLE I  
DIACETYLENIC DIHYDROPEROXIDES

	Dihydroperoxide	M. p., °C.	Carbon		Hydrogen		(O)	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
I	2,7-Dimethyl-3,5-octadiyn-2,7-	95-96.5	60.59	60.51	7.12	7.21	16.1	15.9
II	3,8-Dimethyl-4,6-decadiyn-3,8-	44-45.5	63.70	63.45	8.02	7.45	14.1	13.8
III	7,7'-Dicyclohexyl-7,7'-butadiyn-6,6'-	96-97 dec.	69.04	68.77	7.97	7.95	11.5	11.2
IV	2,4-Hexadiyn-1,6-	Gum <sup>a</sup>	...	...	..	..	22.5	7.6

<sup>a</sup> This gum was difficult to purify.

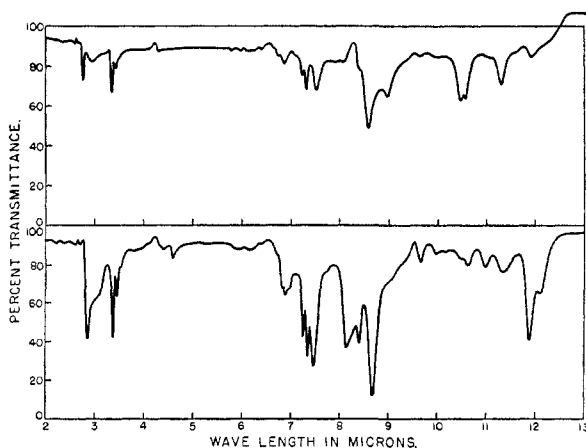


Fig. 1.—Upper curve, infrared spectrum of 2,7-dimethyl-3,5-octadiyn-2,7-diol, 5% in CHCl<sub>3</sub>.

Fig. 2.—Lower curve, infrared spectrum of 2,7-dimethyl-3,5-octadiyn-2,7-dihydroperoxide, 10% in CHCl<sub>3</sub>.

These peroxides have been prepared from the

(1) For paper No. 17, see *Encyclopedia Chem. Technology*, **10**, 58 (1953).

(2) N. A. Milas and O. L. Mageli, *THIS JOURNAL*, **74**, 1471 (1952).

It may be seen from these spectra that the replacement of the hydroxyl groups by hydroperoxy groups produces a new band at about 11.9 μ which is identical with that observed for the monohydroperoxides.<sup>6,7</sup> The bands associated with the hydroxyl groups<sup>5,8</sup> are broadened from 2.7-3.0 μ to 2.7-3.2 μ. This is probably due to a greater association of the hydroperoxy groups as compared to that of the hydroxyl groups. The infrared spectra of the diacetylenic dihydroperoxides show also a very weak band at about 4.6 μ which is due to the presence of acetylenic bonds.

Although the diacetylenic dihydroperoxides are relatively stable at room temperature, they explode on heating with a considerable violence. They are shock sensitive and when detonated with

(3) N. A. Milas, U. S. Patent 2,223,807 (Dec. 3, 1940); N. A. Milas and D. M. Surgenor, *THIS JOURNAL*, **68**, 205 (1946).

(4) E. R. Bell, F. F. Rust and W. E. Vaughan, U. S. Patent 2,573,947 (Nov. 6, 1951).

(5) N. B. Colthup, *J. Opt. Soc. Am.*, **397** (1950).

(6) O. D. Shreve, M. R. Heather, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

(7) A. R. Philpotts and W. Thain, *ibid.*, **24**, 638 (1952).

(8) R. B. Barnes, R. C. Gore, U. Liddel and V. E. Williams, "Infrared Spectroscopy," Reinhold Publ. Corp., New York, N. Y.

a blasting cap they explode with a tremendous brisance.<sup>9</sup>

### Experimental

**2,7-Dimethyl-3,5-octadiyn-2,7-dihydroperoxide (I).**—Into a cold (0°) well-stirred mixture of hydrogen peroxide (85.5 g. of 48%) and sulfuric acid (144 g. of 95.5%) in a tall 400-cc. beaker was added, in small portions, over a 45-minute period, 50 g. (0.3 mole) of 2,7-dimethyl-3,5-octadiyn-2,7-diol, m.p. 131°. The mixture was stirred at 0 ± 5° for 3 hours longer, then diluted with an equal volume of a saturated solution of ammonium sulfate and extracted with ether. The ether extract was dried over magnesium sulfate, filtered and the ether removed under reduced pressure; yield of the crude peroxide, 53 g. (89%), which analyzed for 94% purity. This product was recrystallized from water-ethanol mixtures to give a crystalline peroxide, m.p. 95–96.5°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>: C, 60.59; H, 7.12; (O), 16.1. Found: C, 60.51; H, 7.21; (O), 15.9.

Upon catalytic hydrogenation in glacial acetic acid using platinum oxide as catalyst, the dihydroperoxide consumed 6.8 moles of hydrogen per mole as compared with the calculated value of 6.0. The higher experimental value is probably due to a slow hydrogenolysis of the tertiary hydroxyl groups.

The infrared spectra of the glycol and dihydroperoxide are shown in Figs. 1 and 2.

**3,8-Dimethyl-4,6-decadiyn-3,8-dihydroperoxide (II).**—Into a cold (0°) well-stirred mixture of 14.2 g. (0.20 mole) of 48% hydrogen peroxide and 24.0 g. of 95.5% sulfuric acid was added 50 cc. of reagent grade benzene mixed with 10 cc. of anhydrous ethyl ether. The temperature was maintained at 5–10° and 2.35 g. (0.012 mole) of 3,8-dimethyl-4,6-decadiyn-3,8-diol, m.p. 73–76° (mixed isomers) was added in a single portion. The temperature was kept below 10° for the first 10 minutes, then allowed to rise to room temperature (25°). The whole mixture was stirred for 1 hour longer, after which time all solid had dissolved. An equal volume of saturated ammonium sulfate was then added, the mixture stirred for a little while longer and the benzene-ether layer separated. The non-aqueous layer was extracted once with saturated ammonium sulfate then neutralized with magnesium carbonate. Filtration and removal of the solvent under reduced pressure at room temperature left 2.5 g. (91% yield) of a yellowish oil which analyzed for 12.0% active oxygen (85% of theory). Most of this oil crystallized after standing 2–3 days at –4°. By dissolving the oil in a small amount of benzene, adding a little pentane, and seeding in the cold (–4°) with a crystal of the hydroperoxide, a colorless crystalline product was obtained, m.p. 44–45.5°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>: C, 63.70; H, 8.02; (O), 14.1. Found: C, 63.45; H, 7.45; (O), 13.8.

**7,7'-Dicyclohexyl-7,7'-butadiyn-6,6'-dihydroperoxide (III).**—To a cold mixture (0°) of 14.2 g. (0.2 mole) of 48% hydrogen peroxide and 24 g. of 95.5% sulfuric acid was added a mixture of 60 cc. of benzene and 10 cc. of anhydrous ether. The temperature was maintained at 5–10°. To this mixture was then added with rapid stirring 4.92 g. (0.20 mole) of 7,7'-dicyclohexyl-7,7'-butadiyndiol-6,6', m.p. 173°. The reaction temperature was then allowed to rise to room temperature (25°), and after 1 hour of stirring, the solid had completely dissolved. Stirring was con-

tinued for an additional hour, then the non-aqueous layer separated, washed with a saturated solution of ammonium sulfate, followed by neutralization with magnesium carbonate and dried over magnesium sulfate. When the solvent was removed, 4.5 g. (81% yield) of a thick, yellowish oil remained which crystallized into a white solid upon seeding with a few crystals of the peroxide. After washing with pentane and drying at room temperature, this product melted at 91.5–93° dec. and analyzed 94% pure. For further purification this product was recrystallized from benzene-pentane mixtures at –4° into colorless needles; m.p. 96–97° dec.

*Anal.* Calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>: C, 69.04; H, 7.97; (O), 11.5. Found: C, 68.77; H, 7.95; (O), 11.2.

**2,4-Hexadiyn-1,6-dihydroperoxide (IV).**—Into a cold (0°) well-stirred mixture of hydrogen peroxide (2.8 g. of 48%) and sulfuric acid (4.8 g. of 95.5%), 1.5 g. (0.014 mole) of 2,4-hexadiyndiol-1,6, m.p. 112–113°<sup>12</sup> was added in small portions. Stirring was continued for three hours longer at 1–5°, then the product was isolated in the manner followed above. When the ether was removed under reduced pressure a viscous oil (1.5 g.) was obtained which contained about 30% of the expected dihydroperoxide. Attempts to purify this product by crystallization failed because of its relative instability. Further attempts to introduce more active oxygen by longer reaction periods led to the isolation of highly acidic products devoid of peroxidic properties.

**Diacetylenic Glycols.**—In order to save time a modification of the usual oxidative coupling<sup>10,13</sup> of the acetylenic carbinols<sup>14</sup> was used for the preparation of diacetylenic glycols. In this modification hydrogen peroxide was used as the oxidizing agent instead of air or oxygen. As an example of this method the preparation of 7,7'-dicyclohexyl-7,7'-butadiyndiol-6,6' was obtained in 85% yield in 45 minutes instead of 7 hours, the reaction time previously reported.<sup>11</sup>

Into a mixture of 2.5 g. of cuprous chloride and 8.0 g. of ammonium chloride in a 250-cc. 3-necked flask was added 0.5 cc. of concd. hydrochloric acid dissolved in 25 cc. of water. To this mixture was then added with stirring 20 g. (0.08 mole) of 1-ethynylcyclohexanol in 30 cc. of ethanol. The flask was fitted with an outlet tube, thermometer and a dropping funnel which delivered to the bottom of the flask through a capillary tube. To this mixture was then dropped slowly with rapid stirring in the course of 45 minutes, 30 cc. of 30% hydrogen peroxide. The temperature was maintained at 50 ± 5°. The mixture was then cooled to room temperature and extracted with ether and the extract dried over magnesium sulfate. From the ether solution was recovered 19 g. (85.8%) of crude diacetylenic glycol which was washed with 1 N hydrochloric acid and recrystallized from benzene; m.p. 173–174° (lit. 173°).<sup>11</sup>

When this method was applied to the preparation of the other diacetylenic glycols yields of 85–90% were obtained. Purification was effected by recrystallization from benzene-pentane mixtures.

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(9) Experiments by Lucidol Division of Novadel-Agene Corporation.

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(14) The authors wish to express their thanks to Air Reduction Chemical Company for a generous supply of some of the carbinols and glycols used in this research.