

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

**Structure of Peroxides Derived from Cyclohexanone and Hydrogen Peroxide<sup>1</sup>**M. S. KHARASCH<sup>2</sup> AND GEORGE SOSNOVSKY

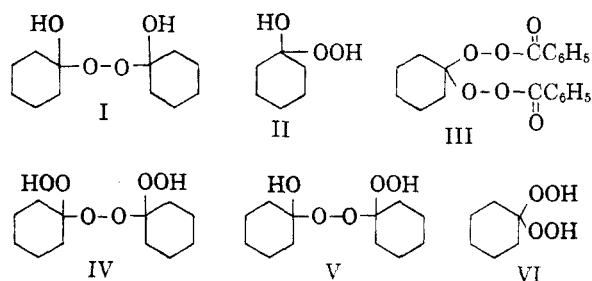
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Cyclohexanone and aqueous hydrogen peroxide react in the absence of a mineral acid catalyst to form 1,1'-dihydroxydicyclohexyl peroxide (I). In the presence of traces of mineral acids, however, the only product is 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide (V). Since I can be converted to V by the action of hydrogen peroxide and traces of mineral acids, I appears to be an intermediate in the formation of V. That 1-hydroxy-1-hydroperoxycyclohexane (II) is also an intermediate in these reactions is suggested by the fact that the 2-chloro and 2-bromo analogs of II certainly are products of the reactions between hydrogen peroxide with the corresponding 2-halocyclohexanones. The decompositions of I and V by ferrous ion have been reinvestigated. Several related peroxides have been prepared, and their infrared spectra recorded.

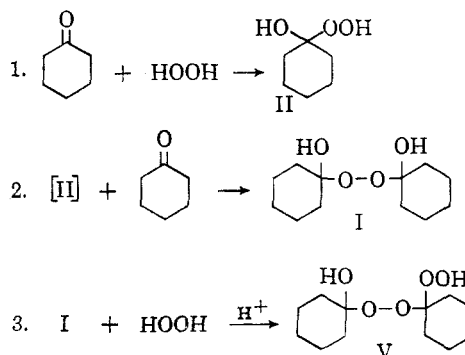
A number of investigators have described the reaction of cyclohexanone with hydrogen peroxide. In 1930 Stoll and Scherrer<sup>3</sup> reported that cyclohexanone and aqueous hydrogen peroxide reacted to form 1,1'-dihydroxydicyclohexyl peroxide (I). The same starting materials in the presence of mineral acid gave a mixture which they believed to consist of I and 1-hydroxy-1-hydroperoxycyclohexane (II). Milas and his co-workers,<sup>4,5</sup> using anhydrous ethereal solutions of cyclohexanone and hydrogen peroxide in the molar ratios of 2:1 and 1:1, obtained two products to which Structures I and II were assigned. Criegee,<sup>6</sup> re-examining this last work, found that, although I reacted with benzoyl chloride (in pyridine) to form benzoyl peroxide, compound II formed III. Oxidation of either I or II with concentrated hydrogen peroxide (84%) gave IV. Guided by these results, as well as by molecular weight determinations and analyses, Criegee concluded that compound I has the indicated structure. For the other product, however, he proposed structure V instead of structure II. More recently, Roedel and his co-workers<sup>7,8</sup> have studied the composition of the "cyclohexanone peroxides"—both the laboratory preparation and the commercial product (Lucidol). They conclude that these peroxides are a mixture of I and V with V as the major constituent. They believe that, in solution, these substances are in a complex equilibrium with their hydrolysis products, one of which is probably VI. This equilibrium product had already been suggested by Criegee<sup>6</sup> and by Cooper.<sup>9</sup>

In spite of the foregoing investigations the condi-

tions leading to formation of either compound I or V remained uncertain; in particular neither I nor II had been established as an intermediate in the formation of V. The present investigation was undertaken in an attempt to settle these questions.



When cyclohexanone is treated with acid-free, aqueous hydrogen peroxide, compound I is the only product, regardless of the ratio of the starting materials. The identity and purity of the products have been established by infrared and active oxygen analysis. The same starting materials in the presence of small amounts of a mineral acid give compound V as the sole product. The infrared spectrum of the crude material thus obtained is indistinguishable from that of the purified product. The following reaction scheme is proposed to account for these observations.



Although intermediate II could not be isolated, the corresponding compounds (VII) derived from 2-chloro- and 2-bromo-cyclohexanone were prepared and characterized. In either the presence or the absence of mineral acid, the 2-halocyclohexa-

(1) This investigation was supported by the Office of Naval Research, Project NR 055-319.

(2) Deceased.

(3) M. Stoll and W. Scherrer, *Helv. Chim. Acta*, **13**, 142 (1930).

(4) N. A. Milas, S. A. Harris, and P. C. Panagiotakos, *J. Am. Chem. Soc.*, **61**, 2430 (1939).

(5) N. A. Milas, U. S. Patent 2,298,405 (1942).

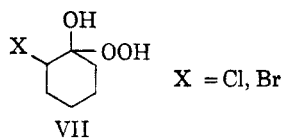
(6) R. Criegee, *Ann.*, **565**, 7, (1949).

(7) M. J. Roedel and co-workers, *J. Am. Chem. Soc.*, **77**, 1756 (1955).

(8) M. J. Roedel, U. S. Patent, 2,601,223 (1952).

(9) W. Cooper and W. H. T. Davison, *J. Chem. Soc.*, 1180 (1952).

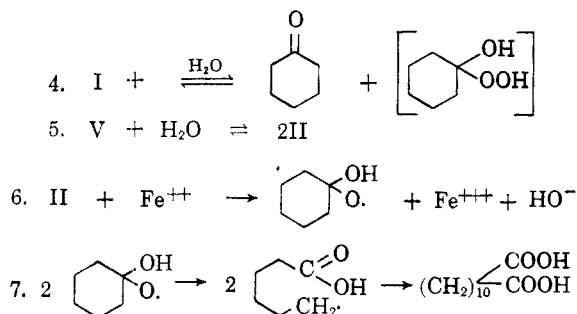
nones react to form only the monomeric hydroxy hydroperoxides. Although these peroxides are too insoluble in benzene to allow their molecular weights to be determined, other analytical data agree well



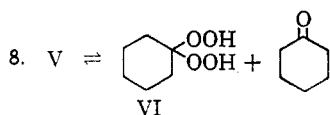
with the proposed structure. The fact that further reaction to form a dimeric peroxide does not occur may be attributed to: (1) the stabilization of VII by the  $\alpha$ -halo substituent (analogous to the stabilization of carbonyl hydrates by electronegative  $\alpha$ -substituents) and (2) the steric hindrance offered by the bulky halogen atoms in the dimeric structure. Molecular models suggest that the latter effect, although not large, may be significant.

A simple method for the preparation of 2-bromocyclohexanone has been developed. All previous preparations of this compound are based on the original procedure of Koetz and Grethe<sup>10</sup>; a slurry of cyclohexanone and calcium carbonate is treated with a stream of carbon dioxide saturated with bromine. This method can however be greatly simplified. When emulsion of cyclohexanone in water is brominated directly, a good yield of bromocyclohexanone is obtained.

The decomposition of compounds I and V by ferrous ion gave 1,12-dodecanedioic acid and cyclohexanone as major products in both cases.<sup>11</sup> However, the yield of acid from compound I was about half of that from compound V. To explain these results it may be assumed that compounds I and V are hydrolyzed prior to the attack by ferrous ions.



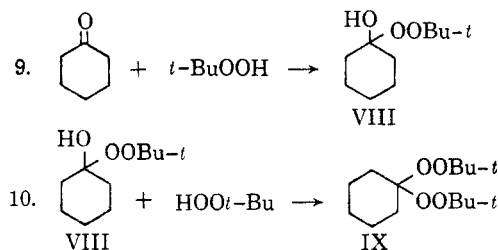
Compound V may be in an equilibrium with compound VI also, particularly, if dissociation occurs before hydrolysis:



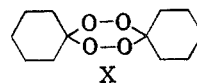
(10) A. Koetz and T. Grethe, *J. prakt. Chem.*, **80**, 473 (1909).

(11) Under similar conditions 1-hydroxy-2-chlorocyclohexyl hydroperoxide was decomposed to a dichloro-1,12-dodecanedioic acid. The position of the chlorine atoms has not yet been established with certainty.

The hypothetical *gem*-dihydroperoxide (VI) has never been isolated; Criegee, however, prepared its dibenzoyl derivative. Another derivative was prepared during the course of the present investigation. When *tert*-butyl hydroperoxide is stored with cyclohexanone or with compound I at room temperature for several months, a very explosive product is formed. On the basis of the molecular weight and infrared spectrum of this substance, structure IX is proposed for it.<sup>12</sup> Its formation may perhaps proceed through a hemiacetal intermediate (VIII):



Cyclohexanone peroxides when decomposed form a number of other products. Cooper<sup>13</sup> has shown that compound V gives 1,12-dodecanedioic acid, cyclohexanone, and hexanoic acid. Dilthey<sup>14</sup> isolated polymeric 6-hydroxyhexanoic acids from the products formed by the acid catalyzed decomposition of cyclohexanone peroxide. Stoll and Scherrer,<sup>3</sup> by treating a solution of cyclohexanone peroxide in alcohol with concentrated sulfuric acid, obtained the ester of 6-hydroxyhexanoic acid. In the present study it has been found that, in the presence of perchloric acid, V decomposes to give a mixture of high-boiling acids and dicyclohexylidene diperoxide (X).



The decomposition of cyclohexanone peroxides by ferrous ion gives, in addition to cyclohexanone and 1,12-dodecanedioic acid, a mixture of liquid products which appears to consist of hexanoic, hydroxyhexanoic, and polymerized hydroxyhexanoic acids. Small quantities of caprolactone were isolated from this mixture. Although the formation of these by-products in the absence of ferrous salts may be interpreted by an ionic mechanism,<sup>15</sup> a free radical mechanism is favored for this reaction in the presence of ferrous salts. In order to demonstrate that the liquid acids formed under the latter conditions are not derived from the acid-catalyzed decomposition of the peroxides, V was decomposed by dilute

(12) This compound was prepared by the acid-catalyzed condensation of *tert*-butyl hydroperoxide with cyclohexanone by F. H. Dicket, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **71**, 1432 (1949).

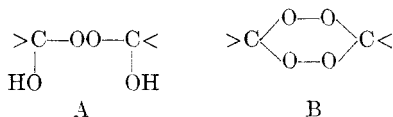
(13) W. Cooper, *J. Chem. Soc.*, 1341 (1951).

(14) W. Dilthey, M. Inckel, and H. Stephan, *J. prakt. Chem.*, **154**, 219 (1940).

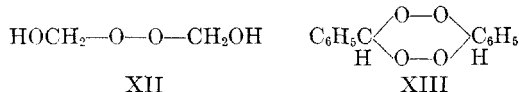
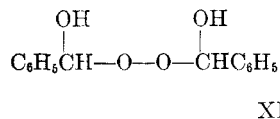
(15) M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 150 (1951).

sulfuric acid at room temperature. Only cyclohexanone (75% yield) was identified.

In recent years a number of publications<sup>16-20</sup> dealing with the infrared spectra of various peroxides have appeared. However, as yet, very few spectra of compounds containing the groups A or B have been reported.



In the present work, several representative compounds of these classes have been prepared and their spectra recorded. Because of the instability of these substances in solution, KBr disks were employed for the determination of their spectra. In spite of this precaution, the spectrum of bis(1-hydroxybenzyl) peroxide (XI) showed some carbonyl absorption. On account of the extreme sensitivity to heat and friction of bis(hydroxymethyl) peroxide (XII), its spectrum was determined in chloroform solution. The preparation of compounds XI and XII was reinvestigated. Benzaldehyde and 30% hydrogen peroxide gave a product (XI) melting at 86.5°; Nef's product<sup>21</sup> melted at 60-62°. A more detailed procedure (based on the method originally proposed by Wieland<sup>22</sup>) was developed for the preparation of XII.



As other authors have found, no single infrared absorption band suitable for the identification of unknown peroxides can be chosen. However, the spectra of these substances can be used successfully to establish the identity and purity of known products. For future reference, the spectra of the more difficultly accessible peroxides are presented in Figure 1.

#### EXPERIMENTAL<sup>23</sup>

*Analytical determination of ketone peroxides.* Powdered sodium iodide (ca. 1 g.) was dissolved in glacial acetic acid

(16) G. J. Minkoff, *Proc. Roy. Soc. London*, **224**, 176 (1954).

(17) R. W. Foreman and H. P. Lankelma, *J. Am. Chem. Soc.*, **79**, 409 (1957).

(18) O. D. Shreve, H. B. Knight and co-workers, *Anal. Chem.*, **23**, 282 (1951).

(19) A. R. Philpotts and W. Thain, *Anal. Chem.*, **24**, 639 (1952).

(20) M. R. Leadbeter, *Compt. rend.*, **230**, 829 (1950).

(21) J. U. Nef, *Ann.*, **298**, 292 (1898).

(22) H. Wieland and A. Wingler, *Ann.*, **431**, 301 (1923).

(23) Melting and boiling points are uncorrected.

(ca. 30 ml.) under an atmosphere of nitrogen gas. Whenever a small amount of iodine was liberated, the solution was carefully decolorized with the minimum amount of sodium thiosulfate solution. The peroxide (0.2-0.3 g.) was weighed on an analytical balance, dissolved in a minimum amount of isopropyl alcohol, and added to the iodide reagent. After a few minutes the liberated iodine was titrated with 0.1N sodium thiosulfate solution. This method is also applicable to the determination of hydroperoxides.

*1,1'-Dihydroxydicyclohexyl peroxide (I).* To stirred cyclohexanone (49 g., 0.5 mole) at room temperature, hydrogen peroxide (30%, 28 ml., 0.25 mole) was added. The mixture became slightly warm and homogeneous. After 1 hr. during which stirring was continued, an oil separated and slowly solidified. The solid (51 g., 90%) was crushed under water, collected on a filter, and thoroughly washed with water. Further purification was difficult since the compound decomposed partially during recrystallization, m.p. 69-71° (methanol-ether).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{22}\text{O}_4$ : C, 62.58; H, 9.63; active oxygen, 7.0%. Found: C, 62.50; H, 9.60; active oxygen, 6.7%.

*1-Hydroxy-1'-hydroperoxydicyclohexyl peroxide (V).* (a) *Criegee's procedure.*<sup>8</sup> A mixture of cyclohexanone (19.6 g., 0.2 mole) and 2N hydrochloric acid (2 ml.) was treated with hydrogen peroxide (30%, 22.6 ml., 0.2 mole) as described above. The crystalline mass was recrystallized from glacial acetic acid at 50-60°, washed with 50% acetic acid, and dried at 0.1 mm. Hg for 12 hr. The product (15 g., 62%) melted at 76-77°.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{22}\text{O}_5$ : C, 58.51, H, 9.00; molecular weight, 246; active oxygen, 13.0%. Found: C, 58.67; H, 8.85; molecular weight, 250 (cryoscopic in benzene); active oxygen, 12.7%.

(b) *From commercial cyclohexanone peroxide (Lupercol JDB-85).* Commercial cyclohexanone peroxide (50 g.) was dissolved in methanol (500 ml.), and water (300 ml.) was immediately added to this solution. After a few minutes, crystallization commenced. The solid (27 g., 54%) was collected on a filter, washed with water (200 ml.), and dried in a vacuum desiccator over sodium hydroxide at 2 mm. Hg, m.p. 76-77°.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{22}\text{O}_5$ : C, 58.51; H, 9.00. Found: C, 58.43; H, 8.70.

*Infrared spectrum:* identical with that of an authentic sample of 1-hydroxy-1'-hydroperoxy dicyclohexylperoxide (preparation described above).

(c) *From 1,1'-dihydroxydicyclohexyl peroxide (I).* 1,1'-Dihydroxy dicyclohexylperoxide (11.5 g., 0.05 mole) was mixed with 30% hydrogen peroxide (12 ml., 0.1 mole) in the presence of 2N hydrochloric acid (ca. 3 ml.). After a few minutes the slurry solidified. The product (8.5 g., 69%) was filtered and thoroughly washed with water. A small portion (1 g.) was recrystallized from a mixture of glacial acetic acid (2 ml.) and water (1 ml.), m.p. 76°.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{22}\text{O}_5$ : C, 58.58; H, 9.00; molecular weight, 246; active oxygen, 13.0%. Found: C, 59.00; H, 9.18; molecular weight, 250; active oxygen, 13.5%.

*1-Hydroxy-2-chlorocyclohexyl hydroperoxide (VII, X = Cl).* A mixture of 2-chlorocyclohexanone<sup>24</sup> (13.1 g., 0.1 mole) and 30% hydrogen peroxide (11.3 ml., 0.1 mole) was shaken for 0.5 hr. During this period the temperature rose to about 40°. The reaction mixture became homogeneous after standing for ca. 12 hr. The reaction mixture was concentrated by removal of water at 2-mm. Hg pressure and room temperature. The resulting slurry was mixed with a solution of benzene in petroleum ether, and the product was collected on a filter. The white product was washed several times with a benzene-petroleum ether mixture. The combined mother liquors were concentrated and worked up in a similar manner. The solid (13.5 g., 92%) melted at 76°.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{11}\text{O}_3\text{Cl}$ : C, 43.20; H, 6.62; Cl, 21.3;

(24) M. S. Newman, M. D. Farbman, and H. Hipsher, *Org. Syntheses*, **25**, 22 (1945).

active oxygen, 9.65%. Found: C, 42.83, H, 6.82; Cl, 21.5; active oxygen, 8.90%.

This product is practically insoluble in petroleum ether, slightly soluble in benzene, and soluble in ether or acetone. When stored at room temperature, the compound decomposed, liberating hydrochloric acid. From the resultant liquid, adipic acid was isolated, m.p. 150°; the melting point of a mixture with an authentic sample showed no depression.

**2-Bromocyclohexanone.** To a stirred mixture of cyclohexanone (33 g., 0.34 mole) and water (100 ml.), bromine (54 g., 0.34 mole) was added over a period of 3 hr., during which the temperature was maintained between 25 and 30° by external cooling. Stirring was then discontinued, and the heavy organic layer was separated from the aqueous layer. The aqueous layer was extracted with ether, and the ethereal extracts combined with the organic layer. The solution was dried over calcium chloride; ether was removed at reduced pressure, and 2-bromocyclohexanone (40 g., 67%) was obtained by distillation, b.p. 96–99°/18 mm.;  $n_D^{20}$  1.5120.

**1-Hydroxy-2-bromocyclohexyl hydroperoxide (VII, X = Br).** A mixture of 2-bromocyclohexanone (36 g., 0.2 mole) and 30% hydrogen peroxide (25 ml., 0.2 mole) was shaken for about 1 hr. During this period the reaction mixture became warm, and when allowed to stand overnight it became homogeneous. When the walls of the vessel were scratched, a solid separated. The crystalline mass was mixed with a solution of benzene in petroleum ether and collected on a filter. The mother liquor was concentrated at reduced pressure and more of the solid was recovered. The combined white solid (30 g., 70%) was recrystallized from benzene, m.p. 82–83° (dec.).

*Anal.* Calcd. for  $C_6H_{11}O_3Br$ : C, 34.16; H, 5.22; Br, 37.95; active oxygen, 7.5%. Found: C, 34.27; H, 5.26; Br, 37.80; active oxygen, 8.4%.

**1,12-Dodecanedioic acid.** (a) *Decomposition of 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide by ferrous ion.* A solution of ferrous sulfate heptahydrate (14 g., 0.05 mole) and

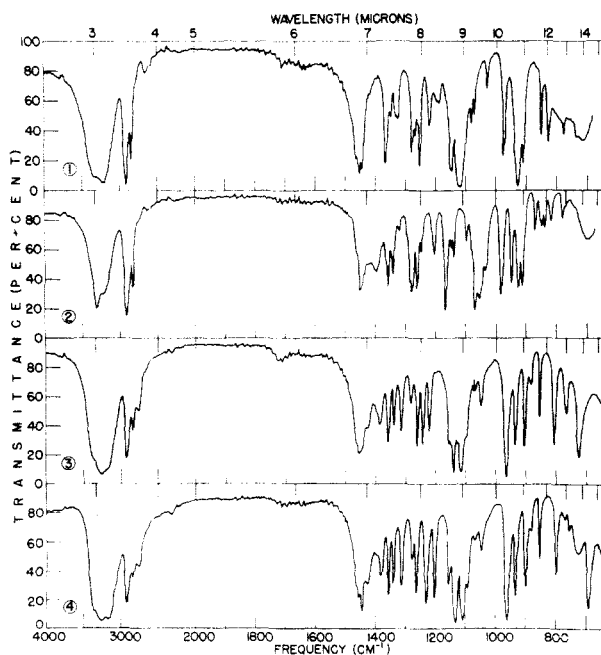


Fig. 1. Infrared absorption spectra of peroxides:

- 1,1'-Dihydroxydicyclohexyl peroxide (KBr disk)
- 1-Hydroxy-1'-hydroperoxy dicyclohexyl peroxide (KBr disk)
- 1-Hydroxy-2-chlorocyclohexyl hydroperoxide (KBr disk)
- 1-Hydroxy-2-bromocyclohexyl hydroperoxide (KBr disk)

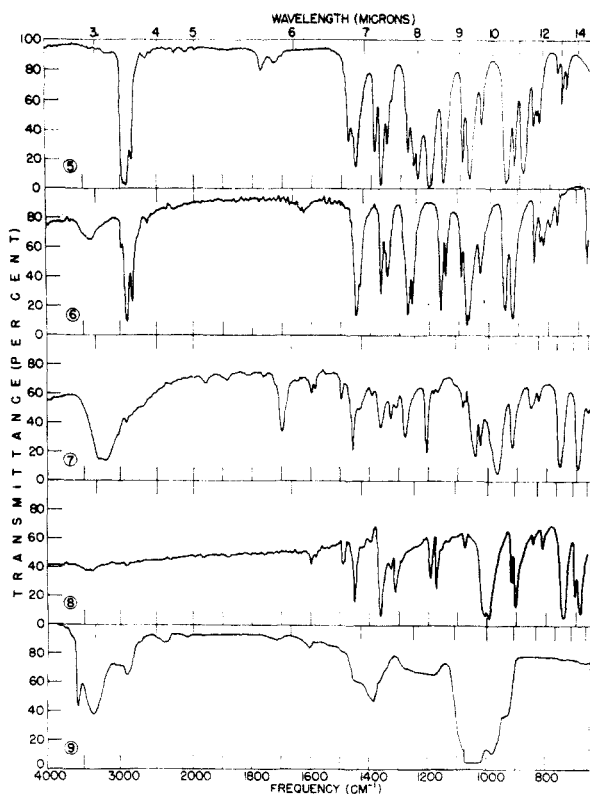


Fig. 2

5. 1,1-Di-*tert*-butylperoxy cyclohexane (pure liquid)
6. Dicyclohexylidene diperoxide (KBr disk)
7. Bis(1-hydroxybenzyl) peroxide (KBr disk)
8. Dibenzaldiperoxide (KBr disk)
9. Bis(hydroxymethyl)peroxide (1%  $CHCl_3$  solution, 1-mm. cell)

concentrated sulfuric acid (1 ml.) in water (25 ml.) was added rapidly to a stirred solution of the peroxide (6.2 g., 0.025 mole) in methanol (80 ml.) under an atmosphere of nitrogen gas. The exothermic reaction was moderated by external cooling with ice water. After 0.5 hr. the reaction mixture was diluted with water (200 ml.) and acidified with sulfuric acid to pH 1. The mixture was then extracted with 4*N* sodium hydroxide, washed with water, and dried over sodium sulfate. After removal of ether by distillation cyclohexanone (1.25 g., 26%) was recovered; 2,4-dinitrophenyl hydrazone, m.p. 155°. The alkaline extract was acidified with sulfuric acid, and the liberated acids were taken up in ether. After removal of the ether at reduced pressure, a white solid remained; this was washed thoroughly with petroleum ether to remove liquid impurities. After recrystallization from methanol-ether, the pure acid (2.2 g., 38% yield, based on starting material) melted at 127–128°.

*Anal.* Calcd. for  $C_{12}H_{22}O_4$ : C, 62.58; H, 9.63. Found: C, 62.30; H, 9.30%.

(b) *Decomposition of 1,1'-dihydroxydicyclohexyl peroxide.* The procedure described in the preceding experiment was employed. The peroxide (5.9 g., 0.025 mole) gave cyclohexanone (2.8 g., 54%) and 1,12-dodecanedioic acid (1.2 g., 20%). From the liquid portion a substance was isolated by distillation, b.p. 98–100°/2 mm.;  $n_D^{20}$  1.4510. This substance may be caprolactone.

*Anal.* Calcd. for  $C_6H_{10}O_2$ : C, 63.13; H, 8.83. Found: C, 63.00; H, 9.26.

**Dichloro-1,12-dodecanedioic acid.** An aqueous solution of ferrous sulfate heptahydrate (6 g. in 15 ml. water) was rapidly added to a stirred solution of 1-hydroxy-2-chlorocyclohexyl peroxide (3.3 g., 0.02 mole) in methanol (10 ml.). The exothermic reaction was moderated by external

cooling with ice water. A solid phase (ferric salt of the organic acid) separated from the reaction mixture. After decantation of the liquid, this solid mass was moistened with methanol, and sulfuric acid was added to liberate the organic acid. The acidic solution was extracted with ether and the ether layer, in turn, was extracted with 2*N* sodium hydroxide. The alkaline extract was acidified, and the crude acid (1.9 g.) was collected on a filter, washed thoroughly with petroleum ether, and recrystallized from a mixture of methanol and ether, m.p. 117–118°.

*Anal.* Calcd. for  $C_{12}H_{20}O_4Cl_2$ : C, 48.20; H, 6.70; Cl, 23.42; molecular weight, 298. Found: C, 48.32; H, 6.78; Cl, 23.44; molecular weight, 295 (Rast).

*Hydrolysis of compound V.* Dilute sulfuric acid (20%, 60 ml.) was added to a stirred solution of V (10.2 g., 0.042 mole) in methanol (160 ml.) at room temperature. The reaction mixture was diluted with water, and saturated with sodium chloride. Cyclohexanone (6 g., 75%) was extracted with ether, b.p. 155°.

*Dicyclohexylidene diperoxide (X).* A 30% solution of hydrogen peroxide (28 ml., 0.25 mole) was added at room temperature to cyclohexanone (24.5 g., 0.25 mole). After 15 min., glacial acetic acid (50 ml.) was added; then a solution of perchloric acid (10%) in glacial acetic acid (3 ml.) was also added. When the reaction mixture was warmed on a steam bath, a precipitate was formed. The reaction mixture was then diluted with water, and the solid (3.9 g., 14%) was collected on a filter. The product, after recrystallization from methanol, melted at 127–128°.

*Anal.* calcd. for  $C_{12}H_{20}O_4$ : C, 63.13; H, 8.83%. Found: C, 63.4; H, 8.90%. Cyclohexanone (8.2 g.) was recovered from the aqueous reaction mixture.

*Bis(1-hydroxybenzyl)peroxide (XI).* Benzaldehyde (10.6 g., 0.1 mole) was mixed with hydrogen peroxide (30%, 5.7 ml., 0.05 mole). The temperature rose to about 30°, and, after a few hours, crystals separated from the reaction mixture. These crystals were collected and washed with petroleum ether. The mother liquor was treated with an additional portion of hydrogen peroxide (5.7 ml., 0.05 mole). When the mixture thus formed was allowed to stand overnight, more crystals separated. This crystalline product was collected on a filter, washed with petroleum ether, and combined with the first crop of crystals obtained (total 11 g., 90%). Since the combined product was found to decompose on standing, the sample was thoroughly washed with petroleum ether, immediately prior to analysis, m.p. 86.5° (melting point reported by Nef,<sup>21</sup> 60–62°).

*Anal.* Calcd. for  $C_{14}H_{14}O_4$ : C, 68.28; H, 5.73%. Found: C, 68.40; H, 5.97%.

*1,1-Di-tert-butylperoxycyclohexane (IX).* (a) A mixture of cyclohexanone (10 ml., ca. 0.1 mole) and *tert*-butyl hydroperoxide (9.1 g., 0.1 mole) was stored for about 3 months at room temperature. The reaction mixture was then distilled at reduced pressure. *In view of the highly explosive nature of this mixture every possible precaution should be taken during this entire operation. Despite precautionary measures, an attempt to analyze 7 mg. of this substance for carbon and hydrogen resulted in a violent explosion which shattered the combustion tube.* Molecular weight: Calcd. for  $C_{14}H_{28}O_4$ : 260. Found: 262 (cryoscopic in benzene). Infrared max.: 1390<sup>-1</sup>, 1365<sup>-1</sup> (*t*-butyl group); no carbonyl or hydroxy group absorption.

(b) *From 1,1'-dihydroxydicyclohexyl peroxide.* A mixture

of 1,1'-dihydroxydicyclohexyl peroxide (5.8 g., 0.025 mole) and *tert*-butyl hydroperoxide (16 g., 0.18 mole) was stored for several months at room temperature. The reaction mixture was carefully distilled at reduced pressure. The product (5 g., b.p. 52–54°/0.15 mm.,  $n_D^{20}$  1.4395) appeared to be identical with that of the preceding experiment. This identity was confirmed by comparison of the infrared spectra.

*Bis(hydroxymethyl)peroxide (XII).* (a) *Preparation of ethereal formaldehyde solution.* A mixture of aqueous formaldehyde (38%, Merck, 100 ml.) and ether (200 ml.) was refluxed for a few minutes. The ether layer was separated and dried over sodium sulfate. For analysis the following procedure was employed: 0.1*N* sodium hydroxide solution (0.1*N*, 20 ml.) and 3% hydrogen peroxide (ca. 10 ml.) were added to the ethereal solution (0.5 ml.). The mixture was warmed on a steam bath until gas evolution ceased (ca. 30 min.). Excess sodium hydroxide was then titrated with 0.1*N* hydrochloric acid. The concentration of formaldehyde in the ethereal solution was found to be 4.3%.

(b) *Preparation of ethereal hydrogen peroxide solution.* 30% hydrogen peroxide (100 ml.), excess ether (200 ml.), and anhydrous sodium sulfate were mixed and thoroughly shaken in a separatory funnel. The ethereal solution was separated and its hydrogen peroxide content determined as follows: A small portion of the solution (2 ml.) was added to iodide reagent (potassium iodide, 1 g.; concentrated sulfuric acid, 30 ml.; and water, 200 ml.). The liberated iodine was titrated with a 0.1*N* sodium thiosulfate solution. The concentration of hydrogen peroxide in the ethereal solution was found to be 2%.

A mixture of the ethereal formaldehyde solution (140 ml., 0.2 mole) and the hydrogen peroxide solution (180 ml., 0.1 mole) was concentrated by removal of ether at reduced pressure. When the ether had been removed, the pressure was reduced to 0.1 mm. Hg and the mixture was maintained at room temperature for several hours to remove all traces of moisture. The resulting thick oil was chilled in Dry Ice, and the walls of the container were gently scratched. The peroxide crystallized slowly. Anhydrous ether was then added and the reaction mixture was allowed to stand at 0° for several hours. Then the crystalline product (2.5 g.) was collected by rapid filtration, washed with ice cold ether, pressed gently between filter papers, and dried for several hours at 0.1 mm. Hg, m.p. 62.5°.

*Anal.* Calcd. for  $C_2H_6O_4$ : C, 25.54; H, 6.43. Found: C, 25.69; H, 6.30%.

It should be noted that the product is sensitive to heat and friction.

*Dibenzaldiperoxide (XIII).* The procedure of Baeyer and Villiger<sup>25</sup> was followed. A sample of the product was purified for analysis by solution in chloroform, followed by precipitation with methanol, m.p. 202°.

*Anal.* Calcd. for  $C_{14}H_{12}O_4$ : C, 68.84; H, 4.95%. Found: C, 68.90; H, 5.2%.

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