3.06 (1 H, m), 2.39–1.75 (1 H, m), 1.67–1.34 (3 H, m), two overlapping triplets centered at 1.19 (2.34 H, t, J = 7 Hz) and 1.13 (0.66 H, t, J = 7 Hz), 1.06–0.72 (1 H, m), 0.66–0.21 (2 H, m); mass spectrum m/e (rel intensity) 114 (6), 97 (19), 86 (14), 79 (6), 73 (12), 72 (100), 68 (15), 67 (17), 57 (14), 44 (59), 43 (51), 41 (41).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.66; H, 9.90.

***trans*- and *cis*-3-Methoxy-1-methyl-2-oxanorcarane (*trans*- and *cis*-3c).** Treatment of 5.05 g (24 mmol) of a 80:20 mixture of *trans*- and *cis*-3-methoxy-1-methyl-2-oxa-7,7-dichloronorcarane (*trans*- and *cis*-**2c**) as described above for *trans*-**2a**, except that 945 mg (135 mg-atoms) of lithium was used, afforded a 80:20 mixture (analyzed by GLC) of *trans*- and *cis*-**3c** which distilled together, yielding 2.10 g (62%) of a colorless oil: bp 145–155° (760 mm); ir (film) 3080, 3010, 2960, 2880, 2840, 1450, 1365, 1240, 1210, 1120, 1100, 1040, 1010, 970, 920, 900, 880, 855 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.31 (0.8 H, t, J = 3 Hz, equatorial anomeric proton), which overlaps slightly with 4.23 (0.2 H, d of d, J = 2.5 and 7 Hz, axial anomeric proton), 3.31 (2.4 H, s), 3.28 (0.6 H, s), 2.25–1.76 (1 H, m), 1.75–1.32 (3 H, m), 1.29 (3 H, s), 1.00–0.52 (1 H, m), 0.51–0.25 (2 H, m); mass spectrum m/e (rel intensity) 142 (M^+, 0.7), 114 (8), 112 (5), 111 (12), 72 (20), 71 (18), 67 (14), 58 (100), 55 (8), 45 (15), 43 (55), 41 (24).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.31; H, 9.87.

***trans*- and *cis*-3-Ethoxy-1-methyl-2-oxanorcarane (*trans*- and *cis*-3d).** Treatment of 3.32 g (14.8 mmol) of a 95:5 mixture of *trans*- and *cis*-3-ethoxy-1-methyl-2-oxa-7,7-dichloronorcarane (*trans*- and *cis*-**2d**) as described above for *trans*-**2a**, except that 640 mg (91 mg-atoms) of lithium was used, afforded a 95:5 mixture (analyzed by GLC) of *trans*- and *cis*-**3d** which distilled together, yielding 1.80 g (78%) of a colorless oil: bp 170–175° (760 mm); ir (film) 3080, 3010, 2970, 2880, 1460, 1380, 1250, 1120, 1105, 1055, 1030, 965, 930, 890, 860, 840 cm^{-1}; NMR (100 MHz, CCl_4) δ 4.45 (ca. 0.95 H, t, J = 3 Hz, equatorial anomeric proton), slightly detectable apparent quartet at ca. 4.34 (ca. 0.05 H, axial anomeric proton), two overlapping quartets centered at 3.78 (1 H, d of q, J = 7 and 10 Hz), two overlapping quartets centered at 3.38 (1 H, d of q, J = 7 and 10 Hz), 2.33–1.76 (1 H, m), 1.70–1.35 (3 H, m), 1.30 (3 H, s), 1.19 (ca. 2.85 H, t, J = 7 Hz) superimposed on 1.15 (ca. 0.15 H, t, J = 7 Hz), 1.03–0.60 (1 H, m), 0.54–0.27 (2 H, m); mass spectrum m/e (rel intensity) 156 (M^+, 2), 141 (1), 128 (25), 112 (17), 111 (28), 99 (8), 95 (8), 93 (15), 86 (39), 72 (100), 67 (24), 57 (23), 55 (25), 44 (46), 43 (79), 41 (24), 39 (14).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 68.90; H, 10.29.

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Registry No.—*trans*-**2a**, 30823-17-7; *trans*-**2b**, 30823-19-9; *cis*-**2b**, 30823-18-8; *trans*-**2c**, 55123-04-1; *cis*-**2c**, 55089-06-0; *trans*-**2d**, 55123-05-2; *cis*-**2d**, 55089-07-1; *trans*-**3a**, 55298-07-2; *trans*-**3b**, 55298-08-3; *cis*-**3b**, 55332-71-3; *trans*-**3c**, 55255-15-7; *cis*-**3c**, 55298-09-4; *trans*-**3d**, 55255-16-8; *cis*-**3d**, 55298-10-7; lithium, 7439-93-2.

References and Notes

(1) Part IV in a series "The Chemistry of 2-Alkoxy-3,4-dihydro-2*H*-pyrans". Part III: A. J. Duggan and S. S. Hall, *J. Org. Chem.*, in this issue.
(2) Taken in part from the Ph.D. Thesis of A.J.D. which was submitted to the Graduate Faculty, Rutgers University, Oct 1974.
(3) (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); (b) *ibid.*, **81**, 4256 (1959); (c) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).
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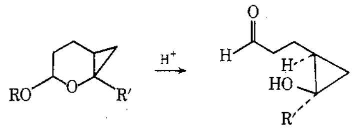
(6) The potential advantages of using sodium benzoate as a quenching agent for metal–ammonia reductions was first suggested by (a) M. Smith in R. L. Augustine, Ed., "Reduction", Marcel Dekker, New York, N.Y., 1968, p 105; and successfully applied in (b) S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); (c) S. S. Hall, *J. Org. Chem.*, **38**, 1738 (1973).
(7) Hydrolysis of these compounds, using the method described in ref 4a, would yield the corresponding cyclopropanol. The overall sequence, then, should provide a selective procedure to synthesize these unique structures.



(8) The ir spectra were determined with a Beckman Model IR-10 infrared recording spectrophotometer. The NMR spectra were determined at 100 MHz with Varian Associates Model XL-100 and Model HA-100 NMR spectrometers. The chemical shifts are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Consolidated Electronics Corp. Model 110-21B mass spectrometer.

An Improved Synthesis of Dicyclohexylidene Diperoxide

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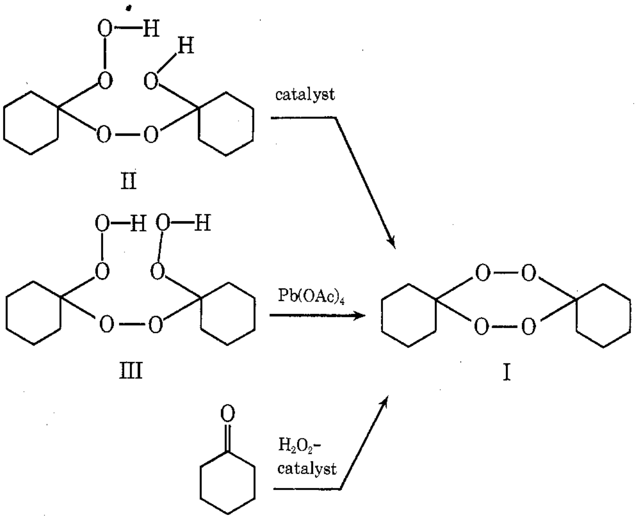
Dicyclohexylidene diperoxide (I) has been prepared by the "dehydration" of 1-hydroxy-1′-hydroperoxydicyclohexyl peroxide (II)[1,2] and by reaction of 1,1′-dihydroperoxydicyclohexyl peroxide (III) with lead tetraacetate.[3-5] Dicyclohexylidene diperoxide (I) has also been prepared "directly" from cyclohexanone and hydrogen peroxide[6] (Scheme I).

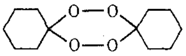
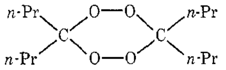
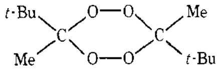
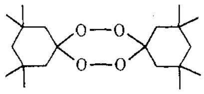
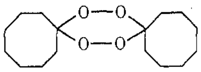
Scheme I



The disadvantages of preparing diperoxides such as I from the "open" peroxides such as II and III follow. For optimum results, the intermediate open peroxides should be purified by recrystallization before use. In general, "open" peroxides are more hazardous to work with owing to the shock sensitivity of these materials. The yields of the diperoxides prepared using this procedure are generally low.[1-5]

The former procedures for the direct conversion of cyclohexanone to the diperoxide also give low yields. Furthermore, the procedures often give mixtures of I, the triperoxide (IV), and "open" peroxides such as II and III that can be difficult to purify.[6]

Table I
Preparation of Some Alkylidene Diperoxides

Peroxide	Registry no.	Mp (lit.), °C	Yield, %
	183-84-6	128–130 (128–130)[a]	87[b] (84)[c]
	55208-76-9	52–54 (47–48)[d–f]	(89)[c]
	20732-35-8	122–125 (124–125)[e,g,h]	(26)[c]
	55208-77-0	184–186[e,i]	(48)[c]
	5681-37-8	97–98 (98)[e,j,k]	(20)[c]

[a] Reference 6. [b] VPC yield. [c] Isolated yield. [d] Reference 9. [e] Satisfactory combustion analytical data for C, H (±0.35%) were provided. Ed. [f] Mol wt calcd 260, found 270. [g] Mol wt calcd 232, found 200. [h] Reference 10. [i] Mol wt calcd 340, found 373. [j] Mol wt calcd 284, found 293. [k] Reference 11.

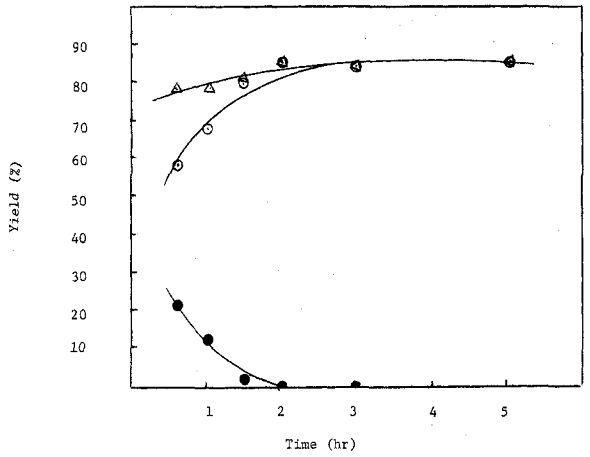
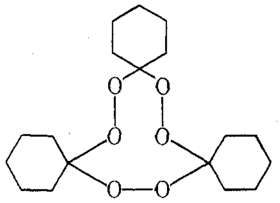


Figure 1. Plot of percent yield of cyclohexanone peroxides vs. time (hours): ●, cyclohexanone triperoxide; ⊙, cyclohexanone diperoxide; △, sum of diperoxide plus triperoxide.



IV

Since dicycloalkylidene diperoxides are useful for the preparation of macrocyclic compounds,[7] an investigation of this synthesis was conducted. After a rather extensive series of experiments in which we varied acids, solvents, temperature, mole ratio, etc., we found that high yields of the diperoxide (I) could be obtained by the reaction of cyclohexanone with hydrogen peroxide in the presence of anhydrous methanesulfonic acid (MSA) using an acetonitrile–methylene chloride solvent system.

Under optimum conditions (given in the Experimental Section), an 87% yield of the diperoxide I has been observed along with only trace amounts of the trimeric peroxide IV and the "open" peroxides II and III. The product can be conveniently isolated to afford pure dicyclohexylidene diperoxide (I) without recrystallization. It should be noted that this procedure greatly simplifies the work-up of the subsequent thermolysis mixture, since the number of components is reduced.

Story and coworkers have shown that, under a variety of conditions, the diperoxide I is formed from the triperoxide IV rather than the dehydration of the "open" peroxide II.[7] The following scheme was proposed (Scheme II).

Scheme II

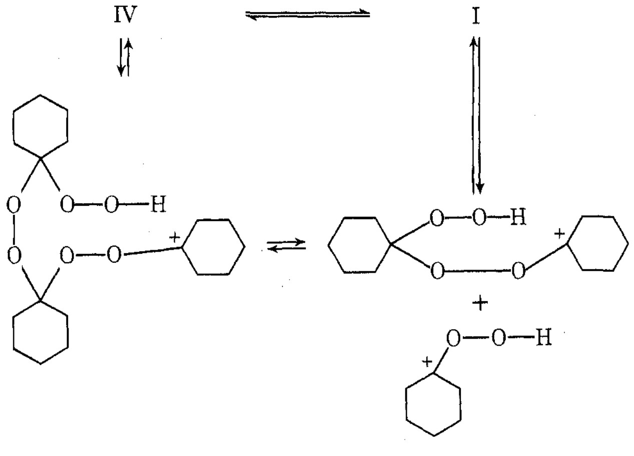
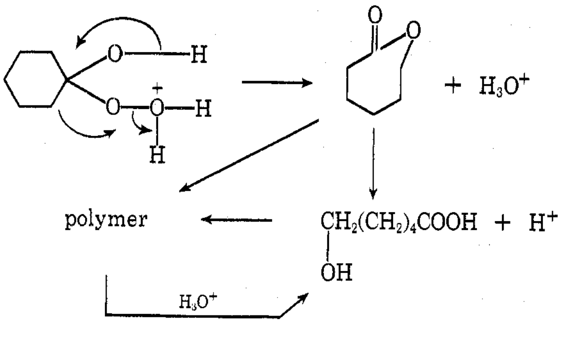


Figure 1 is a plot of the yield of cyclohexanone diperoxide (I) and triperoxide (IV) vs. time. (The initial conditions are given in the Experimental Section.) One notes immediately the high yields of the triperoxide in the early stages of the reaction. It is also very evident that the diperoxide is formed at about the same rate that the triperoxide is destroyed. Furthermore, the diperoxide is much more stable than the triperoxide under the conditions of this series of experiments. This is in agreement with the results previously reported by Story and coworkers.[6] These workers found that, under a variety of conditions, tricyclohexylidene triperoxide (IV) was the kinetic product and dicyclohexylidene diperoxide (I) was the thermodynamic product.

The major by-product from the diperoxide synthesis was caprolactone or products derived from caprolactone (i.e., polycaprolactone or the hydroxy acid). A Baeyer–Villiger-like reaction[8] would account for these products (Scheme III).

Since the procedure was so successful for the preparation of cyclohexanone diperoxide, a few representative ketones

Scheme III



were chosen and an attempt was made to synthesize the diperoxides under essentially the same conditions. The results are shown in Table I. No attempt was made to maximize the yields of any but the first entry in Table I.

In conclusion and summary, the procedure given in this paper is useful for the preparation of high-purity cyclohexanone diperoxide in high yield. Furthermore, there is an indication that the diperoxide I is formed from the triperoxide IV, although one cannot discard the possibility that some of I is formed from the "open" peroxide II. The procedure is also useful for the preparation of peroxides derived from noncyclic ketones as well as cyclic ketones.

Experimental Section

Preparation of Diperoxide. Typical Procedure. Acetonitrile (25 ml) and methylene chloride (25 ml) were placed in a 300-ml round-bottom flask equipped with a stirrer and thermometer. Cyclohexanone (9.8 g, 0.1 mol) was placed in the flask. The mixture was cooled to about 5° and 8 ml of anhydrous methanesulfonic acid was added slowly (small exotherm). Hydrogen peroxide (90%, 3 ml, 0.11 mol) was then added dropwise over about a 10-min period (exothermic). The temperature was maintained at 5° during the addition and during the hold period. At the end of the hold time, 100 ml of water and 100 ml of methylene chloride were added to the reaction mixture. The contents of the flask were transferred to a separatory funnel and the organic and water layers were separated. The water layer was washed with 25 ml of methylene chloride. The methylene chloride was then separated and combined with the first cut. The methylene chloride solution was washed once more with an equal volume of water, dried over anhydrous sodium sulfate, and analyzed for percent cyclohexanone diperoxide and triperoxide by VPC using an internal standard. In some cases an aliquot of the methylene chloride was removed from the sample before it was submitted for VPC analysis and a crude yield of peroxide was obtained. In most cases the crude yield was within a few percent of the yields determined by VPC. The solid peroxide was isolated by removing most of the methylene chloride on a rotary evaporator, adding methanol, and collecting the solid by filtration.

Material Balance Experiment. Methylene chloride (250 ml) was placed in a 1-l. flask along with 250 ml of acetonitrile and cooled to about 5° in a methanol–water–ice bath. Anhydrous methanesulfonic acid (80 ml) was then added slowly (mild exotherm) such that the temperature did not rise above 10°. Hydrogen peroxide (90%, 30 ml, 1.1 mol) and cyclohexanone (98.1 ml, 1.0 mol) were then added simultaneously (slowly) to the stirred mixture by means of two addition funnels. The temperature was maintained within ±2° of 5°. Addition of cyclohexanone required about 45 min. Addition of hydrogen peroxide required about 25 min. The mixture was kept at about 5° and checked for "open" peroxide by TLC. Only a trace of "open" peroxide remained after 2 hr.

Methylene chloride (300 ml) was then added along with 200 ml of water. The mixture was transferred to a separatory funnel and shaken, and the organic and water layers were separated. The water layer was washed with 50 ml of methylene chloride and this was combined with the first cut. The methylene chloride was washed with 300 ml of saturated bicarbonate solution and dried over magnesium sulfate. An aliquot was withdrawn for VPC analysis. The crude yield of isolated dimer was 84%. By VPC the yield was 87.1% dimer and 0.1% trimer.

After filtration of the dimer, an oil was isolated (16 g, 14 wt %) which still contained some dimer–trimer (TLC). By ir, this oil appeared to be mainly a polymer of hexanolactone. (Some 6-hydroxyhexanoic acid was also present). VPC indicated that there was less than 1% cyclohexanone remaining.

VPC Assay for Dicyclohexylidene Diperoxide and Tricyclohexylidene Triperoxide. Although the peroxides are thermally unstable, they can be successfully chromatographed at temperatures below 150° using on-column injection into glass columns that have been silynized. The yields for dicyclohexylidene diperoxide and tricyclohexylidene triperoxide reported in this paper were determined on a 10 ft × 0.375 in. glass column packed with 0.1% OV-17 on glass beads 60–80 mesh. Methyl stearate was used as an internal standard.

Acknowledgment. We would like to thank Story Chemical Corp. for permission to publish this work.

Registry No.—Cyclohexanone, 108-94-1; 4-heptanone, 123-19-3; 3,3-dimethyl-2-butanone, 75-97-3; 3,3,5,5-tetramethylcyclohexanone, 14376-79-5; cyclooctanone, 502-49-8; hydrogen peroxide, 7722-84-1; acetonitrile, 75-05-8; methylene chloride, 75-09-2; methanesulfonic acid, 75-75-2.

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Synthesis and Identification by Shift Reagents of Isomeric 2-Methyl-2-*n*-propylcyclopentane-1,3-diols

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During research aimed at pinpointing the relationships between configuration and activity in meprobamate-type substances, it was necessary to obtain, as starting products, the three 2-methyl-2-*n*-propylcyclopentane-1,3-diol isomers (**4–6**). Their synthesis and structure determined by NMR spectra in the presence of Eu(DPM)$_3$ are reported here.

Chemistry. Sodium borohydride reduction of 2-methyl-2-allylcyclopentane-1,3-dione[1] gave the expected mixture of three isomeric diols, **1**, **2**, and **3**, that were separated by column chromatography. Further catalytic reduction with hydrogen afforded, in nearly quantitative yield, **4**, **5**, and **6** (Scheme I). This method was preferred to the one involving a previous reduction of the allyl group as it gave better yields and easier chromatographic separations.

To obtain the corresponding 4,5-unsaturated compounds, 2-methyl-2-*n*-propyl-4-cyclopentene-1,3-dione (**8**) was synthesized. Yet reduction of **8** with sodium borohydride or lithium aluminum hydride afforded the known mixture of saturated diols **4–6** because of the prevalence of 1,4 over 1,2 addition (Scheme I).

Structure Determination. No compound of the **1–3** and **4–6** series gives the characteristic reactions of the cis diols, probably owing to the considerable steric hindrance