ml). Removal of solvent then furnished 1-acetylcyclohexanol (10), 136 mg (61%), as a colorless liquid: ir (film) 3600–3150, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.3–2.0 (m, 10 H), 2.27 (s, 3 H), 3.65 (br s, 1 H, exchanges with D_2O).

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Registry No.—**3**, 58873-40-8; **4**, 34965-67-8; **5**, 58917-11-6; **6**, 58917-12-7; **7**, 58873-41-9; **8**, 58873-42-0; **9**, 58873-43-1; **10**, 1123-27-9; 2-methoxyvinyllithium, 42722-80-5; estrone methyl ether, 1624-62-0; 1-hydroxy-1-(α-methoxyvinyl)cyclohexane, 54123-63-6; *p*-nitrobenzenesulfinyl chloride, 13088-17-0; *m*-chloroperbenzoic acid, 937-14-4.

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(6) At 130 °C, the sample began to darken rapidly after heating in the melt ca. 90 s and rearrangement was still incomplete. At 100 °C, the melt did not become darkened even upon heating for over 1 h.

Macrocycles. Synthesis and Thermal Decomposition of 3-Benzosuberone Diperoxide

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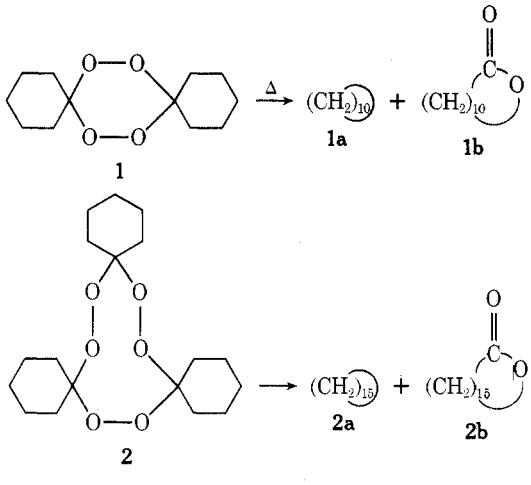
The synthesis and pyrolysis of 3-benzosuberone diperoxide (**4**) gave a fair yield of the macrocyclic hydrocarbon (**5**) and the lactone (**6**). The hydrocarbon (**5**) was converted to 1,6,11,16-tetraketocyclocosane (**9**) using conventional synthetic procedures.

It has been previously reported that cyclic ketone peroxides such as dicyclohexylidene diperoxide (**1**) and tricyclohexylidene triperoxide (**2**) are precursors to macrocyclic hydrocarbons (**1a, 2a**) and macrocyclic lactones (**1b, 2b**).[1] The reactions are illustrated in Scheme I.

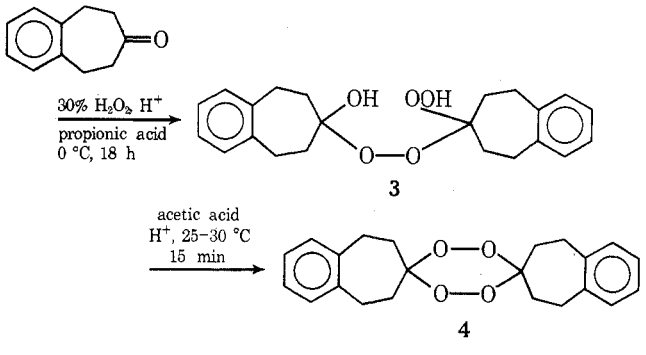
Scheme I



The thermal decomposition of these peroxides was found to give higher, more reproducible yields of the macrocyclic products than photolysis and these results were reported.[2] Improvements have also been reported on synthesis of the precursor triperoxide,[3] diperoxides,[4] and mixed triperoxides.[5]

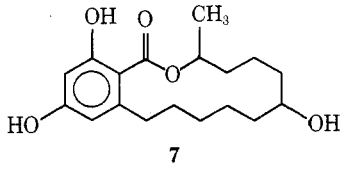
As an extension of the earlier work reported by Story and co-workers,[1] we have undertaken a study of the thermal decomposition of a variety of cyclic ketone peroxides for the purpose of macrocyclic synthesis. In this note, we wish to report our results on the synthesis and thermal decomposition of 3-benzosuberone diperoxide (**4**). The synthesis of this peroxide is outlined in Scheme II.

Scheme II



4 was decomposed in refluxing hydrocarbon solvent to yield the macrocyclic products shown in Scheme III. The products (**5** and **6**) were isolated by a combination of vacuum distillation and column chromatography.

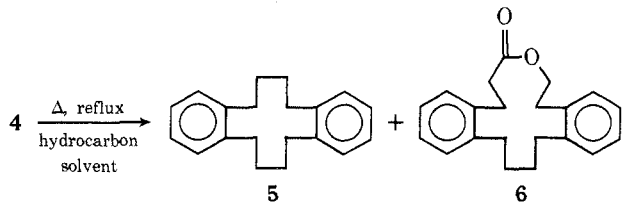
This work greatly extends the utility of the macrocyclic synthesis[1] because it suggests a new approach to the synthesis of molecules similar to animal growth regulators.[6-10] For example, zeranol (**7**) has been used to improve the growth in livestock.[8,9]



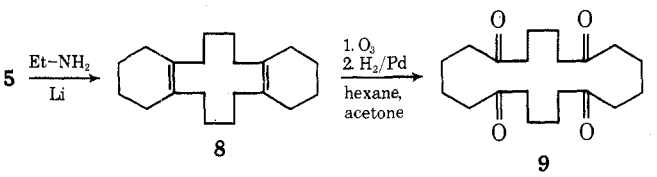
5 was converted by the known procedures shown in Scheme IV to 1,6,11,16-tetraketocyclododocosane (**9**). **9** was tested and found to be unsuccessful as a selective ion reagent.[11]

In conclusion, the synthesis of **5, 6,** and **9** would be difficult to accomplish by conventional syntheses alone. Indeed, the procedures outlined in this paper may be used to synthesize a variety of novel large-ring compounds.

Scheme III



Scheme IV



Experimental Section

Benzosuberone was prepared according to the procedure by Allinger.[12]

Preparation of 1-Hydroxy-1′-hydroperoxydibenzosuberyl Peroxide (3). Benzosuberone (110 g, 0.625 mol) and 30% hydrogen peroxide (71.3 g, 0.625 mol) were dissolved in 300 ml of propionic acid and cooled to 0 °C. Perchloric acid (10%, 20 ml) was added and the solution stirred at 0 °C for 18 h. Water (400 ml) was added to the mixture and the crystals were filtered and washed well with water. The crystals were air dried to yield 103 g (90%) of 1-hydroxy-1′-hydroperoxydibenzosuberyl peroxide (3), mp 114–116 °C. After recrystallization three times from benzene, the melting point was 122–123 °C.

Ir (KBr) 3380 (s), 3250 (s), 3070 (w), 2950 (s), 2860 (m), 1490 (m), 1440 (s), 1390 (m), 1335 (w), 1265 (m), 1230 (w), 1210 (m), 1170 (w), 1140 (w), 1080 (s), 1030 (s), 980 (s), 940 (m), 920 (m), 900 (m), 875 (m), 760 (s), 745 cm^{-1} (s).

Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.31; H, 7.08. Found: C, 71.00; H, 7.08.

Preparation of Benzosuberone Diperoxide[13] (4). To a solution of 5.1 l. of acetic acid and 330 ml of 10% perchloric acid in acetic acid, 66 g of 1-hydroxy 1′-hydroperoxydibenzosuberyl peroxide was added. The temperature was maintained at 25–30 °C. The solid 1-hydroxy-1′-hydroperoxydibenzosuberyl peroxide went completely into solution and the diperoxide (4) precipitated 15 min later (26 g, 40% yield, mp 195 °C). The diperoxide was recrystallized twice from acetone, mp 220 °C.

Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.94; H, 6.86. Found: C, 75.29; H, 7.23.

Pyrolysis of Benzosuberone Diperoxide[14] (4). The following pyrolysis procedures were tried in an attempt to maximize the yields of the macrocyclic products.

(a) Benzosuberone diperoxide (0.50 g) was dissolved in 10 ml of Isopar-K (a hydrocarbon solvent available from Humble Oil) and refluxed for 3 h.

(b) Benzosuberone diperoxide (0.50 g) was dissolved in 10 ml of *n*-decane and refluxed for 3 h.

(c) Benzosuberone diperoxide (0.50 g) was dissolved in 10 ml of Isopar-L (a hydrocarbon solvent available from Humble Oil) and refluxed for 3 h.

(d) Benzosuberone diperoxide (0.50 g) was dropped slowly into an open test tube suspended in an oil bath heated to 230 °C.

The yields were determined by VPC using a 5 ft × 0.25 in. 20% SE-30 column. The yields were as follows.

Procedure	% benzosuberone	% 5	% 6
a	11	13	21
b	10	11	18
c	N.D.	10	13
d	10	9	5

Large-Scale Pyrolysis of Benzosuberone Diperoxide (4). Benzosuberone diperoxide (130 g) was refluxed in 2.6 l. of Isopar-K for 3 h. (Behind a safety shield!). The solvent was removed under reduced pressure. The pressure was reduced to 2.2 mmHg, pot temperature up to 135 °C. Only solvent and benzosuberone were collected up to this time. The pressure was reduced to 0.5 mmHg and the distillate collected at 190–260 °C. The distillate was dissolved in a minimum amount of hexane and placed on the top of a column which contained 500 ml of silica gel. The silica gel was eluted with hexane until no more hydrocarbon could be detected in the elute. The hexane was removed under vacuum and the residue recrystallized from anhydrous ethanol to yield 6.7 g (7% yield) of 1,7-dibenzocyclododecane (5): mp 104–105 °C; ir (CCl_4) 3090 (w), 3055 (w), 3009 (m), 2985 (sh), 2923 (s), 2900 (sh), 2878 (m-s), 1495 (m-s), 1474 (m-s), 1450 (m), 1352 (w), 1343 (w), 1290 (w), 1241 (w), 1175 (w-m), 1056 (w), 1033 cm^{-1} (3).

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.45.

The lactone 6 was eluted from the silica gel column with benzene and recrystallized from absolute ethanol: yield 6%; mp 98–99 °C; ir (CCl_4) 2922 (s), 2850 (m-s), 1715 (s), 1464 (m), 1450 (m), 1413 (m), 1370 (m), 1441 (sh, w), 1372 (w), 1200 (w), 1135 (w-m), 1121 cm^{-1} (w-m).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.93; H, 8.06.

Reduction of 1,7-Dibenzocyclododecane[15] (5). 1,7-Dibenzocyclododecane (5, 6.7 g, 0.025 mol) was placed in a 300-ml, three-necked flask equipped with a thermometer, stirrer, and dry ice condenser. The flask was purged with nitrogen and warmed to drive out moisture. Ethylamine (100 ml) and lithium metal (2.1 g, 0.030 mol) were added. The mixture was stirred for 8 h at reflux temperature and the excess lithium removed. The ethylamine was allowed to evaporate (at room temperature) in the fume hood. Water was added slowly to the residue and the crystals collected, washed with water, and air dried to give 8 (85% yield, mp 95–98 °C). The crude material was recrystallized from absolute ethanol: mp 103–104 °C; ir (CCl_4) 3080 (sh), 2918 (s), 2850 (s), 2814 (m-s), 1469 (m), 1450 (m), 1438 (w-w), 1368 (w), 1347 (w), 1287 (w), 1264 (w-m), 1241 (w), 1163 (w), 1142 cm^{-1} (w).

Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 87.97; H, 12.01.

Preparation of 1,6,11,16-Tetraketocyclodocosane (9). Diolefin 8 (0.65 g) was dissolved in 30 ml of hexane and ozonized at room temperature. A white solid precipitated after several minutes and no more ozone was taken up. (An ir spectrum of the solid showed that the reaction was incomplete.) The hexane was removed; the solid was dissolved in acetone and again ozonized until no more ozone was absorbed.

The acetone solution was hydrogenated at 1 atm pressure and room temperature using 10 mg of palladium on charcoal as catalyst until no more hydrogen was absorbed. The catalyst was filtered and the solvent removed under vacuum. The residue was recrystallized several times from hexane to give 0.090 g (14% yield) of the tetraketone 9: mp 76–77 °C; ir (CCl_4) 2930 (s), 2890 (sh), 2860 (sh), 1712 (s), 1450 (sh), 1438 (m-w), 1408 (m), 1368 (m), 1341 (sh), 1270 (w), 1190 (w), 1164 (w), 1140 cm^{-1} (w).

Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.48; H, 9.55.

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Registry No.—3, 58815-90-0; 4, 58815-91-1; 5, 58815-92-2; 6, 58815-93-3; 8, 58815-94-4; 9, 58815-95-5; benzosuberone, 4443-91-8; hydrogen peroxide, 7722-84-1.

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