H), 1.1–2.7 (m, 7 H), 8.5 (s, 1 H); MS *m/e* 125 (parent and base peak).

Treatment of 1 with Py·HCl in Py. A mixture of 1.75 g (16 mmol) of 1 and 3.7 g (32 mmol) of pyridine hydrochloride (freshly prepared[13]) in 40 ml of dry pyridine was refluxed during 20 h. After extraction, washing with saturated NaCl solution, drying, and evaporation of the organic phase, 1.76 g (76%) of **2** was obtained: bp 103–107 °C (15 mm);[14] ir (CCl_4) 1720 cm^{-1}; NMR (CCl_4) δ 3.45 (m, CH_2Cl); MS *m/e* 148 (isotopic), 146 (parent), 97 (base peak). Treatment of the crude ketone with hydroxylamine hydrochloride afforded exclusively **4**.

Treatment of 3 with Py·HCl in Py. As described above, 2.0 g (16 mmol) of **3** was treated with 3.7 g (32 mmol) of pyridine hydrochloride in 40 ml of pyridine to give 2.0 g (77%) of **4**: bp 80–85 °C (1 mm);[14] NMR (CCl_4) δ 3.45 (m, CH_2Cl); MS *m/e* 163 (isotopic), 161 (parent), 126 (base peak).

Treatment of Bicyclo[4.1.0]heptane, Cyclopropyl Methyl Ketone, and Cyclopropyl Methyl Ketone Oximes with Py·HCl in Py. The title compounds, obtained by WBL, Fluka, and according to a reported procedure,[15] respectively, were treated as above. NMR and GC analyses showed that none of them suffered a detectable transformation.

Treatment of 1 with NH_2OH·HCl in the Presence of Py. A mixture of 2.2 g (20 mmol) of 1 and 2.1 g (30 mmol) of hydroxylamine hydrochloride in 15 ml of ethanol and 15 ml of pyridine was refluxed for 3 h. Water was added and the solution was extracted with ether. Upon washing with 2 N HCl and water, drying, and evaporation of the organic phase 480 mg (15%) of **4** remained as a yellowish oil, purity 85% (GC); the remaining 15% was the ketone **2**.

Treatment of 2 and 4 with 12 M HCl. An equimolar mixture of **2** or **4** and 12 M HCl was shaken for 6 h at room temperature. After the usual work-up the GC and ir analyses showed only the presence of **2** or **4**, respectively.

LiAlH$_4$ Reduction of 4. A solution of 1.92 g (12 mmol) of **4** in 30 ml of anhydrous ethyl ether was added dropwise to a refluxing mixture of 1.8 g (48 mmol) of lithium aluminum hydride in 40 ml of ethyl ether. After 3 h of reflux, work-up, and treatment with ethyl chloroformate,[16] the GC of the urethanes mixture showed two peaks. The product with the shorter retention time (55%) was recognized as **5** on the basis of the GC and GC–MS comparison with an independently prepared sample,[8] MS *m/e* 183 (parent), 140 (base peak). The other product (45%) showed the same retention time and fragmentation pattern as the chlorourethane **6**, one of the two isomers obtained in the catalytic reduction of **4** (see below), MS *m/e* 221 (isotopic), 219 (parent), 90 (base peak).[17]

Catalytic Hydrogenation of 4. A solution of 2.1 g (13 mmol) of **4** in 13 ml of acetic acid (distilled on $KMnO_4$), 6 ml of water, and 2.2 ml of concentrated HCl was hydrogenated at 50 psi at room temperature for 20 h in the presence of 150 mg of PtO_2. The filtrate was extracted and the crude product was treated with ethyl chloroformate[16] to afford 1.96 g (69%) of a 57:43 mixture of **6** and its cis isomer: bp 135–140 °C (1 mm);[14] ir (CCl_4) 3450, 1725 cm^{-1}; NMR (CCl_4) δ 1.2 (t, CH_3 of Et), 4.0 (q, CH_2 of Et), 4.6 (broad, NH), 3.35 (m, CH_2Cl); MS *m/e* 221 (isotopic), 219 (parent), 90 (base peak).[17] If the crude product of hydrogenation was made alkaline and allowed to stand at room temperature for several hours before the treatment with ethyl chloroformate, only **5** and **6** were detected.

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Registry No.—**1**, 5771-58-4; **2**, 57719-96-7; *syn*-**3**, 57719-97-8; *anti*-**3**, 57719-98-9; *syn*-**4**, 57719-99-0; *anti*-**4**, 57720-00-0; **5**, 57720-01-0; **6**, 57720-02-2; **6**, cis isomer, 57720-03-3; hydroxylamine hydrochloride, 5470-11-1; pyridine hydrochloride, 628-13-7; lithium aluminum hydride, 16853-84-3.

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A New Method for the Synthesis of Biscyclododecylidene Cycloalkylidene Triperoxides

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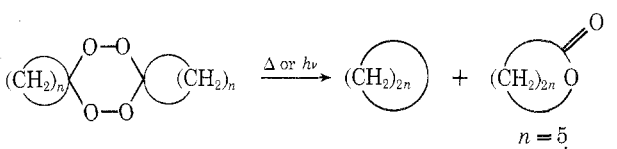
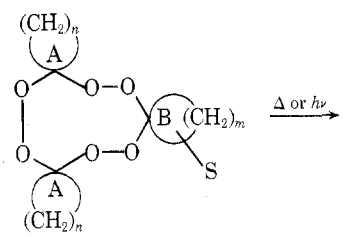
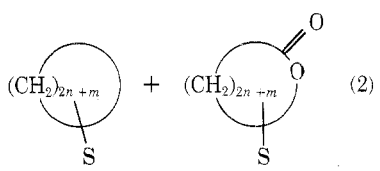
Story and co-workers[1] discovered that the thermal and photochemical decomposition of cyclic ketone peroxides produces macrocyclic lactones and hydrocarbons. This can be illustrated by eq 1 and 2.



(1)



II



(2)

Easy access to the appropriate precursor peroxides constitutes a key step for the synthesis of the desired macrocyclic compounds. Availability of peroxides of type II where $n \neq m$ will obviously broaden the scope of the reaction in terms of varying the size and introduction of the desired functionality in the macrocyclic ring.

A limited number of mixed peroxides of type II have earlier been synthesized by Criegee[2] and the process has been extended by Oldekop[3] and co-workers. Story and co-workers[4] also utilized Criegee's[2] procedure for synthesizing several mixed peroxides. Criegee's procedure essentially consists of treating 1,1′-dihydroperoxydicycloalkyl peroxide with an excess of the appropriate ketone in the presence of anhydrous $CuSO_4$ (eq 3) over an extended reaction period of 1–2 weeks.

Criegee's procedure suffers from the drawback that it

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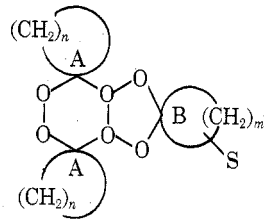
Table I. List of New Cyclic Trimeric Peroxides



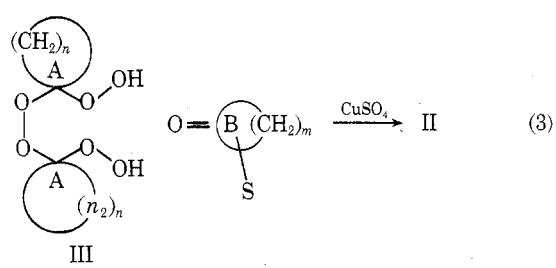
Compd		% yield[a]	Mp, °C	Anal,[c,d] % Calcd	Anal,[c,d] % Found
1	$n = 11, m = 4$	55	178–181 dec	C 70.12 H 10.55	C 69.68 H 10.49
2	$n = 11, m = 5$	30	160–162 dec	C 70.55 H 10.66	C 69.17 H 10.56
3	$n = 11, m = 6$	64	188–190	C 70.95 H 10.66	C 69.89 H 10.99
4	$n = 11, m = 7$	42	185–187	C 71.33 H 10.85	C 70.93 H 10.71
5	$n = 11, m = 10$	10	197–198	C 72.37 H 11.11	C 72.39 H 11.19
6	$n = 11, m = 14$	27	179–183	C 73.54 H 11.39	C 73.77 H 11.53
7	$n = 11, m = 5$	28	141–143	C 70.95 H 10.76	C 70.46 H 10.89
8	$n = 11, m = 5$ S = 4-Me	31	157–161	C 70.95 H 10.76	C 71.39 H 10.71
9	$n = 11, m = 5$ S = 4-Et	27	150–153	C 71.38 H 10.85	C 71.74 H 10.96
10	$n = 11, m = 5$ S = 4-*tert*-butyl	22	157–161 dec	C 72.04 H 11.02	C 72.32 H 11.22
11	$n = 11, m = 5$ S = 4-MeO	15	164–167	C 68.85 H 10.63	C 68.85 H 10.44
12	$n = 11$ B = 2-adamantanone	20	178–180	C 72.56 H 10.39	C 72.01 H 10.49

[a] Yields were not optimized. [b] The peroxides were recrystallized from ethyl acetate–chloroform. [c] Analysis performed by Atlantic Microlab, Inc., Atlanta, Ga. [d] Supplementary ir and NMR data.

Table II. Yield of Macrocyclic Hydrocarbons and Lactones

Peroxide	Hydrocarbon	Yield, %[a] hydrocarbon	Lactone	% yield lactone
$n = 11, m = 4$	Cyclohexacosane	36	Cycloheptacosanolide	14
$n = 11, m = 5$	Cycloheptacosane	34.7	Cyclooctacosanolide	12.3
$n = 11, m = 6$	Cyclooctacosane	30.0	Cyclononacosanolide	12.2
$n = 11, m = 7$	Cyclononacosane	Undetermined	Cyclotriacontanolide	Undetermined

[a] Yields are GC yield. Detailed procedures for the indentification of products and yield determinations are given in ref 7.



III (3)

does not permit the use of solid ketone. Moreover, when Criegee's procedure was used for the synthesis of biscyclododecylidene cyclohexylidene triperoxide (II, $n = 11$, $m = 5$) no detectable amount of the desired product was found even after 3 weeks.

We have developed a simple procedure for the synthesis of biscyclododecylidene cycloalkylidene triperoxides. Table I lists the peroxides synthesized by this procedure. Our procedure essentially consists of slow addition of a solution of 1,1′-dihydroperoxydicyclododecyl peroxide to a solution of the appropriate ketone in the presence of an acid catalyst. A few of the synthesized peroxides ($n = 11$, $m = 4$, 5, 6, 7) were thermolyzed and the products identified by ir and mass spectrometry. Yields of the hydrocarbons and lactones are given in Table II.

This new procedure gives access to a series of mixed triperoxides of type II unknown before and hence to the possibility of synthesizing large-ring compounds which could be synthesized only with difficulty by conventional procedures.[5]

Experimental Section

1,1′-Dihydroperoxydicyclododecyl Peroxide (III, $n = 11$). To a cold (−20 °C) solution of 26.8 g (0.12 mol) of 1,1-dihydroperoxycyclododecane[6] in 550 ml of propionic acid, 7.5 ml of 10% $HClO_4$ in glacial acetic acid was added with stirring. After 1 h at −20 °C, the reaction mixture was maintained at 0 °C overnight. Solid product was filtered off and thoroughly washed with water. Recrystallization from PhH produced pure compounds in 80% yield, mp 151–152 °C (exploded).

Anal. Calcd for $C_{24}H_{46}O_6$: C, 67.0; H, 10.7. Found: C, 67.03; H, 10.7.

Infrared (KBr) 3400 (vs), 2940 (vs, sh at 2850), 1470 (vs, sh at 1445), 1415 (vw), 1385 (m-s, sh at 1350), 1322 (vw), 1300 (vw), 1280 (w), 1260 (m, sh at 1245), 1218 (w), 1190 (vw), 1155 (s, sh at 1170), 1055 (s, sh at 1065 and 1070), 995 (m-s, sh at 1010 and 982), 945 (m-s), 905 (m-w), 870 (m), 855 (w), 840 (vw), 820 (m-w), 795 (m), 740 (m), 710 cm^{-1} (m).

General Procedure for the Preparation of Biscyclododecylidene Cycloalkylidene Triperoxides. To a cold (5–10 °C), vigorously stirred solution of the ketone (100 mmol) in 20–25 ml of PhH containing 30 drops of 10% $HClO_4$ in glacial acetic acid, a $CHCl_3$ solution (1 g, 50 ml) of 1,1′-dihydroperoxydicyclododecyl peroxide was added from a buret (approximately 1 ml/min). After an additional 30–72 h in the cold, most of the solvent was removed at room temperature. On trituration of the residue with methanol, solid material appeared. Filteration and recrystallization from a 2:3 mixture of CH_3COOEt and $CHCl_3$ gave the desired product in reasonably pure condition.

Thermolysis of the Peroxide. Details of the procedure for pyrolysis and identification of the products of pyrolysis are given in the earlier papers.[7]

Ir and NMR Data for Compounds 1–12 (See Table I). Compound 1. Infrared (CCl_4) 2933 (vs), 2860 (w), 2850 (s), 1470 (vs), 1448 (s), 1370 (vw), 1350 (w), 1300 (vw), 1285 (w), 1250 (m), 1220 (m), 1205 (vw), 1192 (w), 1178 (m), 1160 (vw) 1110 (vw), 1080 (s), 1069 (s), 1010 (s), 992 (w), 980 (vw), 955 (m), 915 (w), 880 cm^{-1} (m).

Compound 2. NMR ($CDCl_3$, Me_4Si) δ 1.28 (singlet, sharp) 1.53 (shoulder, broad); Infrared (CCl_4) 2925 (vs), 2860 (vw), 2850 (s), 1470 (vs), 1448 (s), 1360 (w), 1335 (vw), 1325 (w), 1300 (vw), 1285 (vw), 1278 (m), 1265 (vw), 1250 (m), 1220 (m), 1205 (vw), 1192 (vw), 1178 (m), 1170 (m), 1160 (w), 1250 (vw), 1110 (vw), 1092 (w), 1070 (s), 1010 (s), 995 (w), 970 (w), 952 (m), 915 (m), 880 cm^{-1} (m). (m).

Compounds 3. Infrared (CCl_4) 2925 (vs), 2860 (w), 2850 (s), 1470 (vw), 1450 (s), 1370 (w), 1325 (w), 1300 (vw), 1285 (w), 1250 (m), 1220 (m), 1210 (vw), 1195 (vw), 1175 (m), 1160 (vw), 1110 (w), 1080 (v 1078 (s), 1040 (vw), 1015 (s), 970 (vw), 955 (w), 915 (w), 880 cm^{-1} (m).

Compound 4. Infrared (CCl_4) 2925 (vs), 2850 (s, sh at 2860), 1472 (vs), 1448 (s), 1370 (vw), 1352 (w), 1325 (w), 1300 (w), 1285 (w), 1270 (vw), 1250 (m), 1235 (vw), 1220 (m), 1195 (vw), 1178 (m), 1160 (w), 1124 (w), 1110 (w), 1095 (vw), 1070 (s), 1010 (s), 995 (m), 925 (m), 905 (m), 915 (m), 880 cm^{-1} (m).

Compound 5. NMR ($CDCl_3$, Me_4Si) δ 1.37 (shoulder, sharp), 1.50 (shoulder, broad); infrared (CCl_4) 2930 (vs), 2865 (s), 1470 (s), 1440 (s), 1330 (vw), 1255 (m), 1228 (m), 1115 (vw), 1075 (s), 1015 (s), 960 (m), 920 (m), 880 cm^{-1} (m).

Compound 6. NMR ($CDCl_3$, Me_4Si) δ 1.27 (singlet, sharp); infrared (CCl_4) 2930 (vs), 2860 (s), 1468 (s), 1445 (s), 1365 (vw), 13 (vw), 1320 (w), 1245 (m), 1218 (m), 1175 (w), 1165 (m), 1080 (w), 1065 (s), 1005 (s), 968 (w), 950 (m), 910 (w), 870 cm^{-1} (m).

Compound 7. NMR ($CDCl_3$, Me_4Si) δ 0.88, 1.02 (doublet, sharp) 1.23 (singlet, sharp), 1.48 (shoulder, broad); infrared (CCl_4) 2930 (vs), 2860 (s), 1468 (s), 1445 (s), 1365 (vw) 1345 (vw), 1320 (w), 1245 (m), 1218 (m), 1175 (w), 1165 (m), 1105 (vw), 1080 (w), 1065 (s), 1005 (s), 968 (w), 950 (m), 910 (w), 870 cm^{-1} (m).

Compound 8. NMR ($CDCl_3$, Me_4Si) δ 0.82, 0.90 (doublet?, broad), 1.28 (singlet, sharp) 1.52 (shoulder, broad); infrared (CCl_4) 2930 (vs), 2850 (s), 1470 (s), 1445 (s), 1365 (vw), 1350 (w), 1290 (vw), 1250 (m), 1220 (w), 1190 (vw), 1165 (s), 1150 (m), 1078 (vw), 1062 (s), 1045 (w), 1010 (s), 990 (w), 980 (w), 950 (m), 910 (w), 900 (w), 870 cm^{-1} (m).

Compound 9. NMR ($CDCl_3$, Me_4Si) δ 0.80 (singlet, broad), 0.90 (singlet, broad) 1.28 (singlet, sharp), 1.52 (shoulder, broad); infrared (CCl_4) 2930 (vw), 2855 (s), 1470 (s), 1445 (s), 1350 (w), 1325 (w), 1280 (vw), 1245 (w), 1190 (w), 1165 (s), 1110 (w), 1080 (vw), 1062 (s), 1065 (m), 990 (vw), 970 (w), 950 (s), 905 (vw), 870 cm^{-1} (m).

Compound 10. NMR ($CDCl_3$, Me_4Si) δ 0.80 (singlet, sharp), 1.22 (singlet, sharp), 1.50 (shoulder, broad); infrared (CCl_4), 2940 (vs), 2860 (s), 1470 (s), 1445 (m-s), 1365 (m), 1350 (vw), 1320 (vw), 1280 (w), 1240 (w), 1215 (w), 1190 (w), 1172 (w), 1155 (w), 1065 (s), 1005 (m, sh at 990), 950 (m-w, sh at 930), 910 (m-w), 872 (m-w).

Compound 11. NMR ($CDCl_3$, Me_4Si) δ 1.23 (singlet, sharp), 1.50 (shoulder, broad), 3.11 (singlet, sharp); infrared (CCl_4) 2430 (vs), 2860 (s), 2820 (vw), 1470 (vs), 1450 (s), 1370 (w), 1350 (vw), 1325 (w), 1280 (w), 1245 (m), 1320 (w), 1190 (vw), 1175 (vw), 1160 (m), 1145 (w), 1105 (s), 1100 (s), 1080 (vw), 1065 (vs), 1005 (m), 990 (w), 965 (w), 950 (m), 915 (m), 872 cm^{-1} (m).

Compound 12. NMR ($CDCl_3$, Me_4Si) δ 1.23 (singlet, sharp), 1.40–2.30 (complex); infrared (CCl_4) 2930 (vs), 2860 (s), 1470 (s), 1450 (s), 1320 (w), 1285 (w), 1110 (s), 1065 (s), 1015 (s), 1000 (s), 960 (m), 925 (m), 970 cm^{-1} (m).

Registry No.—**1**, 36079-74-0; **2**, 33525-84-7; **3**, 36079-75-1; **4**, 53783-78-1; **5**, 57951-51-6; **6**, 57951-52-7; **7**, 53783-75-8; **8**, 53783-73-6; **9**, 53783-72-5; **10**, 53783-71-4; **11**, 32616-65-2; **12**, 57951-53-8; III (n = 11), 50782-53-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; cycloundecanone, 878-13-7; cyclopentadecanone, 502-72-7; 2-methylcyclohexanone, 583-60-8; 4-methylcyclohexanone, 589-92-4; 4-ethylcyclohexanone, 5441-51-0; 4-*tert*-butylcyclohexanone, 98-53-3; 4-methoxycyclohexanone, 13482-23-0; 2-adamantanone, 700-58-3; cyclohaxacosane, 297-16-5; cycloheptacosane, 297-23-4; cyclooctacosane, 297-24-5; cycloheptacosanolide, 57951-54-9; cyclooctacosanolide, 57951-55-0; cyclononacosanolide, 57951-56-1.

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Bromination of Nitroalkanes with Alkyl Hypobromites

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Recently we reported that methyl hypobromite adds to olefins by an ionic mechanism if the solvent is polar, such as methylene chloride, and in the presence of a radical inhibitor.[1] In another publication we showed that alkyl hypochlorites react with olefins in nitromethane by chlorinating the solvent to give chloronitromethane rather than adding to the olefin.[2] In this reaction the olefin functions as a catalyst. Certain aromatics also catalyze chlorination of nitromethane (naphthalene and the xylenes) while other aromatics react with alkyl hypochlorites in nitromethane to give chloroaromatics.[3]

On the basis of these observations we became interested in determining what type of reaction would occur when alkyl hypobromites are added to olefins in nitromethane. Methyl hypobromite could add to the olefin as occurred with the less polar solvent methylene chloride, or bromonitromethane might be the product, by analogy with the reaction of alkyl hypochlorites in nitromethane. Finally, we considered that it was possible that the polar solvent nitromethane might cause even *tert*-butyl hypobromite to add to olefins by an ionic mechanism.

When *tert*-butyl hypobromite was added to 1-hexene in nitromethane we were surprised to find that in addition to bromonitromethane (**1**), dibromonitromethane (**2**) and tribromonitromethane (**3**) were also formed.

$$CH_2{=}CH(CH_2)_3CH_3 + (CH_3)_3COBr \xrightarrow{CH_3NO_2} \underset{\mathbf{1}}{BrCH_2NO_2} + \underset{\mathbf{2}}{Br_2CHNO_2}$$

$$\underset{\mathbf{3}}{Br_3CNO_2} + (CH_3)_3COH$$

The catalytic role of the olefin, 1-hexene, was established by the fact that no reaction occurred between *tert*-butyl