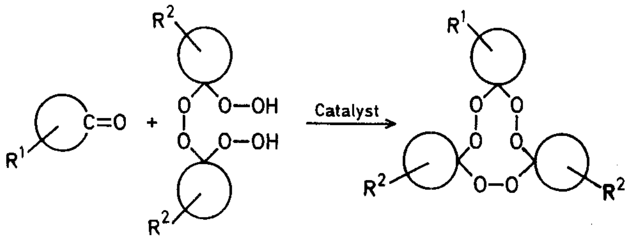
An Improved Synthesis of "Mixed" Alkanone Triperoxides

John R. Sanderson*, Andrew G. Zeiler

Story Chemical Corporation, 500 Agard Road, Muskegon, Michigan 49445, U.S.A.

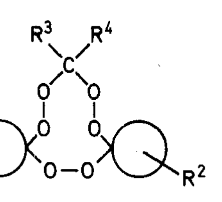
The synthesis of "mixed" triperoxides (**3**) is important because it greatly extends the usefulness of the macrocyclic synthesis by peroxide fragmentation[1,2,3]. The key intermediate in the synthesis of "mixed" triperoxides is the 1,1'-dihydroperoxydicycloalkyl peroxide **2**[2,4,5].



1 **2** **3**

Present syntheses require isolation of **2** and purification by recrystallization[2]. However, it is dangerous to manipulate large quantities of **2** due to the shock sensitivity. In this communication, we wish to report a synthesis of mixed triperoxides which does not require the isolation of **2**. Thus, larger quantities of "mixed" triperoxides may be prepared with a reasonable margin of safety.

The procedure has been extended to the synthesis of the "mixed" triperoxides of the type **4**. Several of these peroxides were prepared initially by Criegee et al.[4].



4

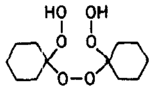
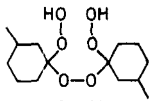
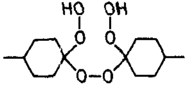
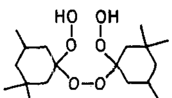
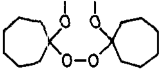
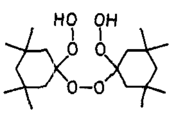
The work described in this communication involves synthesis of **2** in a solvent in which it is soluble (usually benzene). The reaction is conveniently followed by T.L.C.

The procedure was tried on five representative cyclic ketone peroxides to establish the generality of the synthesis. The results are shown in the Table. It should be noted that no attempt was made to maximize the yields of any but the first entry in the Table.

The "mixed" triperoxides **3** or **4** are conveniently synthesized by adding the solution of **2** slowly to a large excess of the appropriate ketone **1** (in the presence of an acid catalyst). Again, the reaction may be monitored by T.L.C. Workup usually affords **3** or **4** in high purity.

1,1'-Dihydroperoxydicyclohexyl Peroxide (2a):
Benzene (1000 ml) was placed in a 2000 ml flask equipped with a stirrer, dropping funnel, and thermometer. Water (100 ml) was added and the solution cooled to 5–10° in an ice-water bath. The mixture was stirred and concentrated sulfuric acid (60 ml) was added slowly enough to maintain the temperature at 5–10°. Hydrogen peroxide (70%, 360 g, 7.4 mol) was then added over a 30–45 min time interval (temperature 5–10°). Cyclohexanone (392 g, 4.0 mol) was added over a 2 h time period (temperature 5–10°). The mixture was then stirred at 0–5° for 1 h and allowed to warm to 15–20° (flask immersed in a water bath). After 20h

Table. Preparation of Some 1,1'-Dihydroperoxydicycloalkyl Peroxides[a] (**2**)

	Peroxide **2**	Purity[b] (%)	Yield[c] (%)	m.p.	m.p. Lit.
a		>95	95,94[d]	80–82°	80–82°[6]
b		>90	n.d.[e]	47–51°	
c		>95	60[f]	131–134°	
d		>90	n.d.[e]	124–127°	
e		>95	56[f]	71–73°	72–73°[7]
f		>95	46[f]	132–134°	

[a] The peroxides were identified by I.R. and ^{1}H-N.M.R.

[b] The purity was estimated by T.L.C.

[c] Yield of isolated product.

[d] Yield determined by iodometric titration.

[e] Difficult to crystallize, small quantity of crystals obtained from hexane after several weeks at 0°.

[f] Yield after one recrystallization from hexane.

at 15–20°, T.L.C. indicated that the reaction mixture was >95% **2a**. Only traces of other peroxides were indicated. The contents of the flask were transferred to a separatory funnel and the lower layer drawn off and discarded. The benzene layer was washed once with water (500 ml) and dried with anhydrous sodium sulfate. An aliquot of the benzene solution was withdrawn and the benzene was removed to yield a white solid; yield of crude **2a**: 95%; m.p. 70–77°. This material was recrystallized once from hexane to yield pure **2a**: m.p. 80–82°. Another aliquot of the solution was withdrawn and analysed for percent **2a** by iodometric titration. This procedure indicated 94% yield.

The *iodometric titration* was carried out by weighing the aliquot to the nearest 0.1 mg and transferring to an iodine flask which contained isopropyl alcohol (50 ml), glacial acetic acid (1 ml) and crushed sodium iodide (0.5–1 g). The solution was heated on a water bath at ~60° for 5 min and titrated with 0.1 *N* thiosulfate. No indicator was used.

Dicyclohexylidene 2-Propylidene Triperoxide (Type **4**, $R^3=R^4=CH_3$):

1,1'-Dihydroperoxydicyclohexyl peroxide (**2a**; a 1 mol aliquot) in benzene was added dropwise (2 h) to a stirred mixture of acetone (500 ml) and 70% perchloric acid (5 ml) cooled to 0–5°. The mixture was stirred at 0–5° for 24 h. Water was added until two layers formed. The layers were separated and the water layer extracted with benzene (100 ml). The benzene extracts were combined and washed with one-third the volume of water. Most of the benzene was removed on a rotary evaporator and methanol added. After two recrystallizations, colorless crystals were collected; yield: 85 g (56%); m.p. 62–65° (Ref.[4], m.p. 63°). The I.R. and ^{1}H-N.M.R. spectra were consistent with a "mixed" triperoxide.

I.R. (CH_2Cl_2): $\nu_{max}=2930$ (s), 2855 (s), 1456 (sh), 1446 (s), 1374 (m), 1363 (s), 1342 (m), 1327 (sh), 1265 (m), 1229 (s), 1200 (s), 1172 (s), 1160 (sh), 1146 (s), 1091 (s), 1062 (s), 952 (s), 926 (sh), 911 (m), 870 (m), 845 (w), 830 (w), 816 cm^{-1} (w).

^{1}H-N.M.R. ($CDCl_3$): $\delta=1.53$ (s), 1.42–1.98 ppm (m).

2-Butylidene Dicyclohexylidene Triperoxide (Type **4**, $R^3=CH_3$, $R^4=C_2H_5$):

The procedure was essentially the same as above. Compound **2a** and butanone (large excess) were used as starting materials: yield of crude product: 77%. The triperoxide could not be purified by recrystallization since it was a viscous oil. I.R., ^{1}H-N.M.R., and molecular-weight determination were consistent with the "mixed" triperoxide.

I.R. (CH_2Cl_2): $\nu_{max}=2970$ (sh), 2943 (s), 2866 (s), 1465 (sh), 1451 (s), 1374 (m), 1362 (m), 1346 (m), 1338 (sh), 1273 (s), 1262 (s), 1229 (m), 1178 (s), 1167 (s), 1148 (sh), 1134 (m), 1096 (s), 1066 (s), 966 (s), 946 (s), 913 (m), 890 (m), 848 (w), 832 cm^{-1} (w).

^{1}H-N.M.R. ($CDCl_3$): $\delta=0.98$ (t), 1.43 (s), 1.22–2.08 ppm (m).

Dicyclohexylidene Cyclopentylidene Triperoxide [Type **4**, $R^3–R^4=–(CH_2)_4–$]:

The procedure was essentially the same as above. Compound **2a** and cyclopentanone were used as starting materials; yield: 56%; m.p. 64–67° (Ref.[2], m.p. 65–67°).

I.R. (CCl_4): $\nu_{max}=2950$ (s), 2878 (m), 2865 (s), 1470 (sh), 1455 (m), 1445 (sh), 1365 (m), 1350 (m), 1330 (m), 1315 (w), 1290 (m), 1278 (m), 1265 (m), 1250 (sh), 1205 (m), 1190 (m), 1166 (m), 1155 (m), 1100 (m), 1090 (sh), 1070 (m), 1035 (w), 985 (m), 960 (s), 930 (m), 915 cm^{-1} (m).

^{1}H-N.M.R. ($CDCl_3$): $\delta=1.54$ (s), 1.60–2.5 ppm (m).

T.L.C. Procedure:

Manganese napthenate (2 g) and *o*-dianisidine (4,4'-diamino-3,3'-dimethoxybiphenyl, 2 g) were dissolved in toluene (100 ml). The solution was stirred and filtered into a spray bottle (solution A). A second spray bottle was filled with 10% hydrochloric acid (solution B).

The peroxides were determined by spotting the unknown on to precoated silica-gel plates along with known standards. The peroxides were chromatographed with hexane/2% acetone. The plates were then sprayed with solutions A and B and heated on a hot plate at 200–250°.

Received: January 31, 1975

---

[1] P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clarke, J. C. Farine, *J. Amer. Chem. Soc.* **90**, 817 (1968).

[2] P. R. Story, P. Busch, *Synthesis* **1970**, 181.

[3] J. R. Sanderson, P. R. Story, *J. Org. Chem.* **39**, 3463 (1974).

[4] R. Criegee, W. Schnorrenberg, J. Becke, *Liebigs Ann. Chem.* **565**, 7 (1949).

[5] Y. A. Oldekop, K. L. Moiseichuk, *Zh. Org. Khim.* **1**, 1934 (1965).

[6] V. L. Antonovskii, A. F. Nesterov, O. K. Lyashenko, *Zh. Prik. Khim.* **40**, 2555 (1967).

[7] B. Lee, *Ph. D. Thesis*, University of Georgia, 1973.