

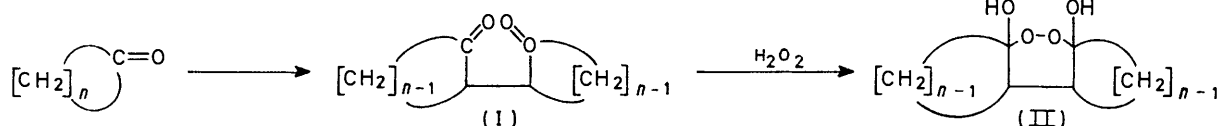
Reactions of Organic Peroxides. Part XX.¹ Peroxides from Bicycloalkyl-2,2'-diones and Hydrogen Peroxide

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Treatment of the bicycloalkyl-2,2'-diones obtained from oxidation by nickel peroxide of cyclopentanone, cyclohexanone, 4-methylcyclohexanone, and cycloheptanone with hydrogen peroxide afforded the corresponding symmetrical dihydroxy-peroxides (3,6-dihydroxy-1,2-dioxans). Perhydrodibenzo[*c,e*][1,2]dioxin-4a,6a-diol gave (i) mainly dodec-6-enedioic acid on reaction with iron(II) sulphate, (ii) the same acid, together with branched-chain dicarboxylic acids, on photolysis, and (iii) a mixture of lactones from treatment with formic acid. Bicyclohexyl-2,2'-dione and *t*-butyl hydroperoxide yielded a symmetrical bis-*t*-butylperoxyperhydrodibenzofuran.

THE formation of a variety of cyclic peroxides from the reactions of hydrogen peroxide with acyclic 1,3- and 1,4-diketones and with *o*-dicarbonyl aromatic compounds has been reviewed.² It has now been found that certain bicycloalkyl-2,2'-diones (I), prepared in high selectivity by

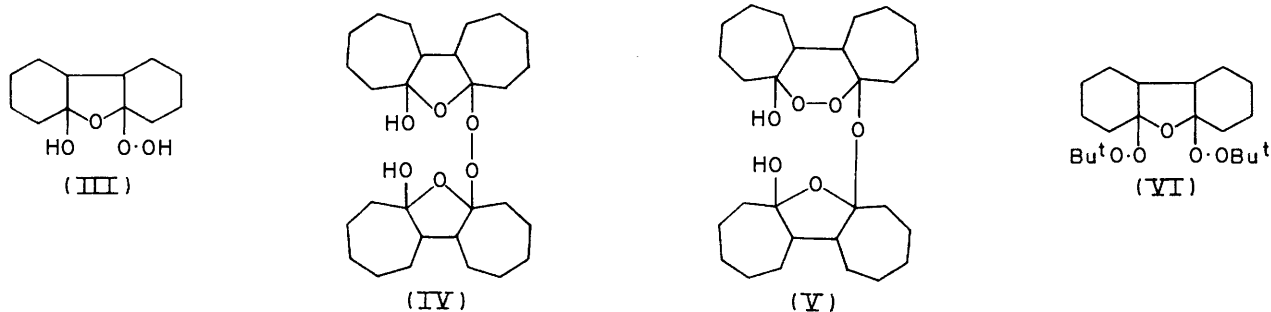
product [either (IV) or (V)]. However, treatment of bicyclohexyl-2,2'-dione with *t*-butyl hydroperoxide yielded the bis-*t*-butylperoxyperhydrodibenzofuran (VI). Evidence for this structure was provided by ¹³C n.m.r. (symmetrical spectrum, with eight signals) and mass



oxidation with nickel peroxide of the corresponding cycloalkanones,³ are converted into solid dihydroxy-peroxides (II) on treatment with aqueous hydrogen peroxide in the presence of traces of base (*e.g.* ammonia).

spectroscopy ($M - H$ fragment), peroxide equivalent, and elemental analysis.

Catalytic hydrogenation of the dihydroxy-peroxide (II; $n = 5$) regenerated the parent diketone which,



The yield of dihydroxy-peroxide (II) in the case $n = 5$ was high, but a lower-melting component isolated from the crude product was an isomer (III), identified from ¹H n.m.r. (two separate OH signals) and ¹³C n.m.r. data [asymmetric structure, with 10 signals; (II; $n = 5$) has six signals]. The dihydroxy-peroxides (II) derived from bicyclopentyl-2,2'-dione ($n = 4$), bicycloheptyl-2,2'-dione ($n = 6$) and 5,5'-dimethylbicyclohexyl-2,2'-dione were obtained in variable but lower yields, and from bicycloheptyl-2,2'-dione there was also isolated a dimeric

although a major product from thermal or base-catalysed decomposition of the peroxide, was then accompanied by dodec-6-enedioic acid (IX). Addition of solutions of this peroxide to iron(II) sulphate gave 60–85% yields of the acid (IX), together with small amounts of the keto-acids

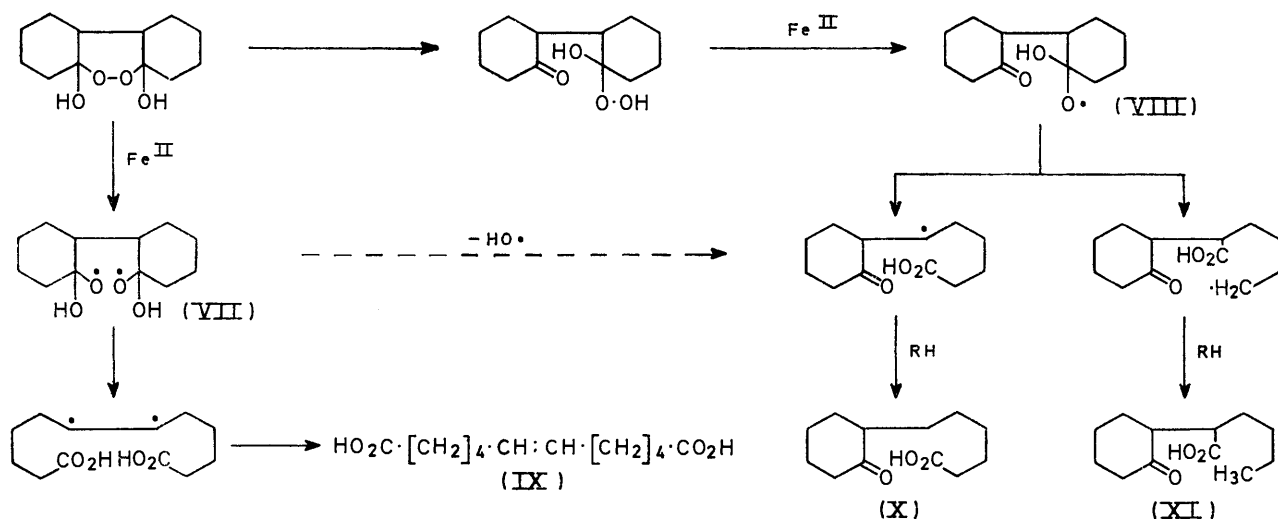
¹ Part XIX, E. G. E. Hawkins, *J.C.S. Perkin I*, 1972, 2882.

² M. Schulz and K. Kirschke, 'Cyclic Peroxides,' in 'Organic Peroxides,' vol. 3, ed. D. Swern, Wiley-Interscience, New York, 1972.

³ E. G. E. Hawkins and R. Large, *J.C.S. Perkin I*, 1974, 280.

(X) and (XI) and the anhydride (XIX); presumably the intermediate radicals (VII) and (VIII) are involved (Scheme 1). Although catalysed or induced scission of the O-O bond to give the diradical (VII) involves no oxidation of Fe^{II}, quantitative experiments showed that

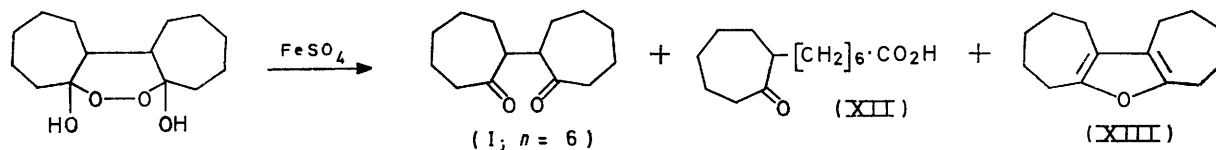
the dimethyl ester of the acid (IX) but, after catalytic hydrogenation and rechromatography, gave peaks due to dimethyl dodecanedioate (C₁₄H₂₆O₄; 36%) and two isomers C₁₄H₂₄O₄ (7 and 19%) considered, on the basis of i.r. and mass spectroscopic evidence, to be esters of a



0.32–0.45 mol. equiv. of Fe^{II} was consumed during this reaction and the use of less than this amount (0.2 mol. equiv.) gave a lower yield (ca. 40%) of the acid (IX).

The dihydroxy-peroxides from bicyclopentyl-2,2'-dione and 5,5'-dimethylbicyclohexyl-2,2'-dione gave

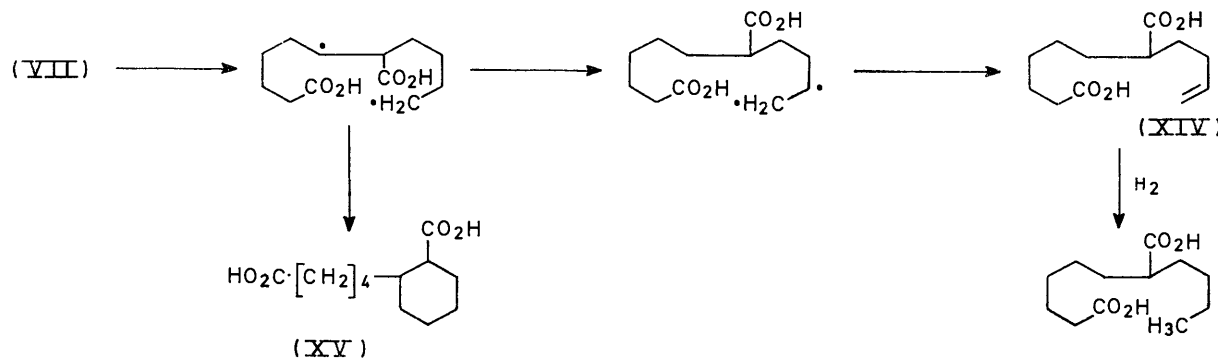
cyclic dicarboxylic acid [possibly (XV)]. The minor component (ca. 20%) was also a mixture of esters (C₁₄H₂₆O₄), but here spectroscopic study indicated the presence of unsaturated, acyclic components with the vinyl isomer (XIV) predominating; hydrogenation gave



mainly the corresponding unsaturated dicarboxylic acids on treatment with iron(II) sulphate, but that from bicycloheptyl-2,2'-dione provided a mixture of the diketone (I; $n = 6$), the keto-acid (XII), and the furan (XIII).

G.l.c. analysis of the methylated product of photolysis

rise to the known dimethyl 2-butyloctanedioate.⁴ The formation of the above products is in accord with Scheme 2, wherein unsymmetrical scission of the diradical (VII) is followed by 1,5-radical rearrangement [to (XIV)] or recyclisation [to (XV)].



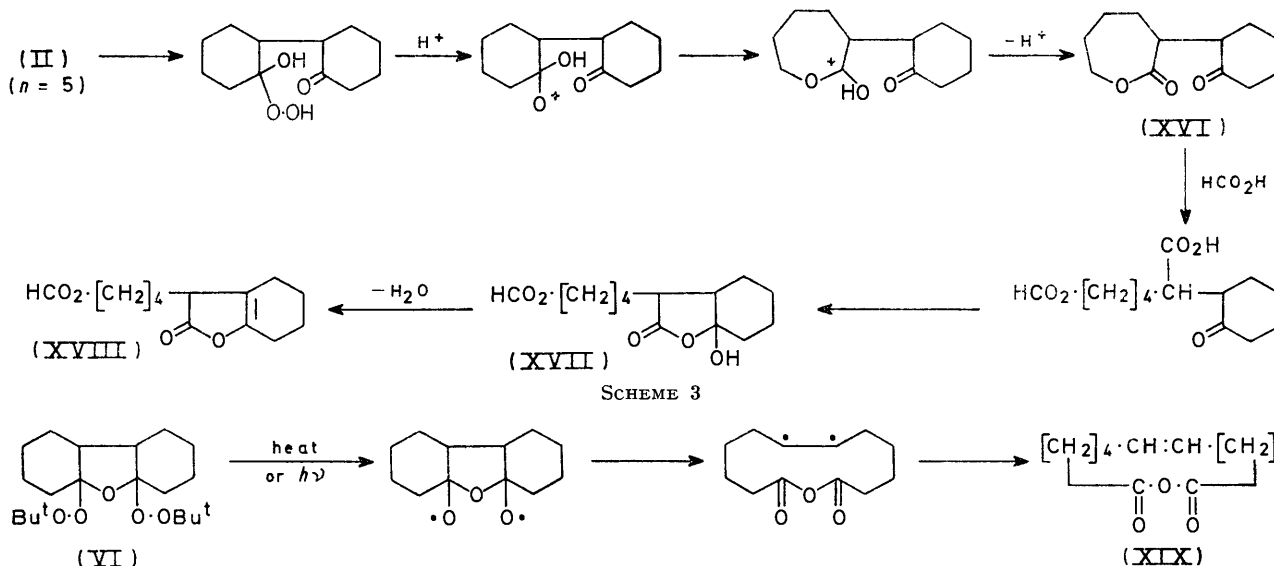
of the dihydroxy-peroxide (II; $n = 5$) appeared to show the presence of two principal components. The major one (ca. 70%) of these behaved chromatographically like

Reaction of the dihydroxy-peroxide (II; $n = 5$) with an excess of formic acid below 20° led to a product from

⁴ E. G. E. Hawkins, *J.C.S. Perkin I*, 1973, 2155.

which was isolated a solid shown to be the keto-lactone (XVI) by i.r. and mass spectroscopy. When the excess of formic acid was removed by distillation, instead of by neutralisation with sodium hydrogen carbonate, the product contained, in addition to (XVI), other lactones with spectra in accord with structures (XVIII) and (XVII) (Scheme 3).

The bis-*t*-butylperoxyperhydrofuran (VI) was not attacked by warm sodium methoxide solution, was re-converted into bicyclohexyl-2,2'-dione with iron(II) sulphate, and decomposed on pyrolysis or photolysis to give mixtures containing the anhydride (XIX).



EXPERIMENTAL

Details of spectroscopic procedures have been reported previously.³ Full mass spectra of the compounds discussed in this paper have been submitted to the Mass Spectrometry Data Centre A.W.R.E., Aldermaston. Results of g.l.c. analyses are quoted as % peak areas.

Perhydrodibenzo[c,e][1,2]*dioxin-4a,6a-diol* (II; $n = 5$).—(i) Crystalline bicyclohexyl-2,2'-dione (1.5 g) was stirred with an excess of 30% hydrogen peroxide, in the presence of ethanol and ammonia (d 0.880; few drops); the solid product was slurried with petroleum and filtered. The crude peroxide (1.45 g; peroxide equiv., 253.8) afforded the *dihydroxy-peroxide* (II; $n = 5$), m.p. 158–160° (from acetone) (Found: C, 62.8; H, 8.75%; peroxide equiv., 235.8. $C_{12}H_{20}O_4$ requires C, 63.2; H, 8.8%; peroxide equiv., 228); ν_{\max} (KBr) 3390 and 3450 cm^{-1} (OH); δ_H [(CD₃)₂SO] 5.6 (2H, s, OH) and 0.9–2.1 (18H, complex, CH and CH₂); δ_C [(CD₃)₂SO] 22.6, 23.7, 25.5, 34.0, 39.9 (C-10a and -10b), and 100.4 (C-4a and -6a); m/e 228 (M , 0.2%), 195 ($C_{12}H_{19}O_2$, 55.6), 177 ($C_{12}H_{17}O$, 31.5), and 41 (100.0).

(ii) Non-crystalline diketone (1.8 g containing 69.3% of low-melting isomer³ by g.l.c.), treated with 30% hydrogen peroxide (2 cm³) and ammonia gave the peroxide (1.9 g), peroxide equiv., 286.5.

(iii) The crude diketone fraction³ (14.0 g; 71.8% pure by g.l.c.) from cyclohexanone–nickel peroxide, stirred with 30% hydrogen peroxide (30 cm³) and ammonia, yielded a crude product (10.5 g), which, recrystallised from ethyl acetate, gave the peroxide (2.9 g), m.p. 153–155°, and 5a-

hydroperoxyperhydrodibenzofuran-4a-ol (III) (1.8 g), m.p. 131–133°, depressed on admixture with the first crop (Found: C, 63.35; H, 8.85%; peroxide equiv., 242.2); ν_{\max} (KBr) 3400 and 3450 cm^{-1} (OH); δ_H (Me₂SO) 0.9–2.0 (18H, complex, CH and CH₂), 5.25 (1H, s, OH), and 5.6 (1H, s, OH); δ_C (Me₂SO) 23.2, 24.1, 25.3, 26.1, 35.2, 37.5, 38.4, 41.1, 99.3 (C-9a or -9b), and 99.8 (C-4a or -5a); m/e 228 (M , 0.1%), 195 (42.9), 177 (25.7), and 41 (100.0).

Perhydrodicyclopenta[c,e][1,2]*dioxin-3a,5a-diol* (II; $n = 4$).—Treatment of crude bicyclopentyl-2,2'-dione fractions³ with hydrogen peroxide (as above) afforded, in variable yield (5–10%), the *dihydroxy-peroxide* (II; $n = 4$) m.p. 106–108° (Found: C, 59.85; H, 8.25%; peroxide

equiv., 203.9. $C_{10}H_{16}O_4$ requires C, 60.0; H, 8.0%; peroxide equiv., 200.0); ν_{\max} (KBr) 3340 cm^{-1} (OH); m/e 167 ($C_{10}H_{15}O_2$, 12.7%), 149 (23.1), and 41 (100.0%).

Perhydrodicyclohepta[c,e][1,2]*dioxin-5a,7a-diol* (II; $n = 6$).—A concentrate (9.3 g) of bicycloheptyl-2,2'-dione,³ similarly treated with hydrogen peroxide, gave a solid (2.0 g) from which the *dihydroxy-peroxide* (II; $n = 6$), m.p. 110–112° (from ether–petroleum) (Found: C, 66.05; H, 9.5%; peroxide equiv., 262.5. $C_{14}H_{24}O_4$ requires C, 65.6; H, 9.4%; peroxide equiv., 265); ν_{\max} (KBr) 3350 and 3500 cm^{-1} (OH); m/e 223 and 205, was isolated. The filtrate, after treatment with petroleum and storage at 0° for 3 days, provided further solid (1.0 g), m.p. 140–141° (from dioxan–acetone) (Found: C, 70.6; H, 9.55%; peroxide equiv., 526.3. Calc. for $C_{28}H_{46}O_6$: C, 70.2; H, 9.7%; peroxide equiv., 478); ν_{\max} (KBr) 3390 and 3440 cm^{-1} (OH); m/e 223, probably either (IV) or (V).

2,9-Dimethylperhydrodibenzo[c,e][1,2]*dioxin-4a,6a-diol*.—A concentrate (17.5 g) of 5,5'-dimethylbicyclohexyl-2,2'-dione,³ treated as above, yielded a crude, solid product (3.6 g) from which was isolated the *dihydroxy-peroxide*, m.p. 161–163° (from ethyl acetate) (Found: C, 65.45; H, 9.8. $C_{14}H_{24}O_4$ requires C, 65.6; H, 9.4%); peroxide equiv., variable; ν_{\max} (KBr) 3400 and 3450 cm^{-1} (OH); m/e 256 (M , 0.3%), 223 (63.0), 205 (30.4), and 55 (100.0).

Reactions of Peroxides with Iron(II) Sulphate.—The *dihydroxy-peroxide* (II; $n = 5$). (i) The peroxide (m.p. 158–160°) [from bicyclohexyl-2,2'-dione (1.0 g)] in dioxan (5 cm³) was added to stirred iron(II) sulphate heptahydrate (2 g) in

water (10 cm³), and the solution was acidified with sulphuric acid and extracted with ether; concentration of the extract provided *trans*-dodec-6-enedioic acid (0.6 g), m.p. 137—139° (from benzene) (lit.,⁵ 134—137°) (Found: C, 63.05; H, 9.1%; acid equiv., 113.5. Calc. for C₁₄H₂₀O₄: C, 63.15; H, 8.8%; acid equiv., 114); ν_{\max} (KBr) 960 (C=C) and 1680 cm⁻¹ (C=O); δ_{H} [(CD₃)₂SO] 1.0—1.8 (8H, m, CH₂ β to C=C or C=O), 1.8—2.4 (8H, m, CH₂ α to C=C or C=O), 5.40 (2H, t, CH=CH); a sharp single resonance (CO₂H) was observed on D₂O addition; *m/e* 228 (C₁₂H₂₀O₄, 0.5%), 210 (C₁₂H₁₈O₃, 25.8), 192 (C₁₂H₁₆O₂, 57.6), and 41 (100.0). Addition of bromine in chloroform yielded 6,7-dibromododecanedioic acid, m.p. 135—138° (from benzene) (Found: C, 36.7; H, 5.05; Br, 41.05%; acid equiv., 190. C₁₂H₂₀Br₂O₄ requires C, 37.1; H, 5.15; Br, 41.25%; acid equiv., 194); *m/e* 307 (*M* - Br), 289, and 271 (C₁₂H₁₆BrO₂).

(ii) The peroxide (17.0 g; peroxide equiv., 243.1) in dioxan (85 cm³) was added to stirred iron(II) sulphate (29.2 g) in water (80 cm³) and dioxan (80 cm³), and the ethereal extract of the acidified product was separated into neutral and acidic components by treatment with sodium hydroxide solution. Examination of the neutral product (0.5 g) by g.l.c.—mass spectroscopy and g.l.c.—i.r. spectroscopy showed the presence of bicyclohexyl-2,2'-dione³ (35.1%), the anhydride (XIX) (8.9%) [ν_{\max} (vapour) 1720 and 1795 cm⁻¹ (C=O, anhydride); *m/e* 210 (*M*, 1.9%), 192 (35.0), 164 (30.0), and 150 (100.0)], and five unidentified components. A portion of the acidic product (14.7 g) was methylated (diazomethane) and shown by g.l.c.—mass spectroscopy, g.l.c.—i.r. spectroscopy, and preparative g.l.c. followed by i.r. and n.m.r. to contain the (\pm)- and *meso*-isomers of the methyl esters of the keto-acid (XI) (19.8%) [ν_{\max} (vapour) 1725 (C=O, ketone) and 1750 cm⁻¹ (C=O, ester); ν_{\max} (CHCl₃) 1715 (C=O, ketone) and 1740 cm⁻¹ (C=O, ester); δ_{H} (CCl₄) 0.9 (3H, t, CMe), 1.1—2.9 (16H, complex, CH and CH₂), and 3.64 (3H, s, OMe); *m/e* 226 (*M*, 5.0%), 129 (18.2), and 98 (McLafferty rearrangement ion, 100.0)], dimethyl dodec-6-enedioate (59.5%) [ν_{\max} (film) 1735 cm⁻¹ (C=O, ester); *m/e* 256 (*M*), 224 (*M* - CH₃OH), and 192 (*M* - 2CH₃OH)] and the methyl ester of the keto-acid (X) (6.6%) [*m/e* 226 (*M*, 0.9%) and 98 (McLafferty rearrangement ion, 100.0)].

Reactions were also run with solutions (or suspensions) of the peroxide in methanol, ethanol, acetone, or ethyl acetate and gave appreciably similar products. In some experiments, with a large excess of iron(II) sulphate and carried out in nitrogen, determinations of the Fe^{II} content showed that 0.32—0.45 mol was consumed per mol of peroxide decomposed, and when 0.2 mol. equiv. of the iron(II) sulphate was initially present the product contained *ca.* 40% of unchanged peroxide. The product (1.6 g) from one of the above experiments, in methanol (1.5 cm³), containing traces of iron(II) sulphate and acetic acid, was hydrogenated at 20—30° over Adams catalyst. G.l.c.—mass spectroscopic and n.m.r. examination of the residue (1.5 g) showed that it contained dimethyl dodecanedioate (*ca.* 70%), bicyclohexyl-2,2'-dione (2.0%), dimethyl 2-n-butyloctanedioate (2.9%) [δ_{H} (CCl₄) 0.9 (t, CMe); *m/e* 259 (*M* + 1, 0.1%), 202 (*M* - C₄H₈, 5.8), 130 (46.5), 87 (100.0), and 74 (20.9%)], (\pm)- (4.6%) and *meso*- (7.0%) isomers of the methyl ester of (XI), and unidentified material (7.8%).

5*a*-Hydroperoxyperhydrodibenzofuran-4*a*-ol (III). The peroxide (3 g) in dioxan (15 cm³) was added to stirred iron(II) sulphate (5 g) in water (20 cm³); the temperature rose to 40°. After the reaction (0.5 h) the product was worked up as in the preceding section (i) to give a product (3.2 g) from

which was isolated *trans*-dodec-6-enedioic acid and an impure acid, m.p. 59—75° (acid equiv., 122.7), probably a mixture of the *trans*- and *cis*- (lit.,⁵ m.p. 62—63.5°) isomers, ν_{\max} (KBr) 730 (C=C), 1690 (C=O), and 3000 cm⁻¹ (CH of CH=CH); δ_{H} [(CD₃)₂SO] 1.2—1.8 (8H, m, CH₂ β to C=C or C=O), 1.8—2.4 (8H, m, CH₂ α to C=C or C=O), and 5.42 (2H, t, CH=CH); a single sharp resonance (CO₂H) was observed on D₂O addition; mass spectrum identical with that of the *trans*-isomer.

The Dihydroxy-peroxide (II; *n* = 4). The peroxide (0.3 g), treated with iron(II) sulphate as above, afforded *dec*-5-enedioic acid (0.2 g), m.p. 112—115° (Found: C, 59.7; H, 7.95%; acid equiv., 100.0. C₁₀H₁₆O₄ requires C, 60.0; H, 8.0%; acid equiv., 100.0); ν_{\max} (KBr) 1685 (C=O) and 960 cm⁻¹ (C=C); *m/e* 200 (*M*, 0.1%), 182 (19.6), 164 (31.2), and 80 (100.0%).

The Dihydroxy-peroxide (II; *n* = 6). The peroxide (1.0 g), under similar conditions, provided a liquid product which, on distillation at 15 mmHg, gave fractions (i) (0.4 g), b.p. 170—200°, and (ii) (0.3 g), b.p. 200—270°, and a residue (0.2 g). Fraction (i) yielded a solid, m.p. 58—62° (from aqueous methanol), consisting mainly of the furan (XIII) [ν_{\max} (KBr) 1580 cm⁻¹ (C=C-C=C); *m/e* 204 (*M*, 100.0%), 175 (25.4), and 150 (44.6)] with some bicycloheptyl-2,2'-dione. Fraction (ii) contained the keto-acid (XII) [ν_{\max} (film) 1700 cm⁻¹ (C=O); *m/e* 112 (C₇H₁₂O, McLafferty rearrangement ion)].

2,9-Dimethylperhydrodibenzo[*c,e*][1,2]dioxin-4*a*,6*a*-diol. Reaction of the crystalline peroxide (0.6 g) with iron(II) sulphate gave a product (0.45 g), b.p. 230—250° at 15 mmHg, from which was isolated 4,9-dimethyldodec-6-enedioic acid, m.p. 86—88° (from benzene) (Found: C, 65.35; H, 9.3. C₁₄H₂₄O₄ requires C, 65.6; H, 9.35%; ν_{\max} (KBr) 965 (C=C) and 1700 cm⁻¹ (C=O); *m/e* 256 (*M*, 0.2%), 238 (9.4), 220 (16.7), and 55 (100.0)].

Other Reactions of the Dihydroxy-peroxide (II; *n* = 5).—(a) *Hydrogenation*. The peroxide (1.6 g) in ethyl acetate (50 cm³) was hydrogenated at room temperature over palladium-charcoal catalyst (uptake 175 cm³ in 0.75 h). Evaporation of the filtered solution left a residue (1.5 g), shown by g.l.c. to consist of a mixture of bicyclohexyl-2,2'-dione isomers.³

(b) *With sodium hydroxide*. The peroxide (1.0 g) was heated with aqueous sodium hydroxide on a water-bath for 0.5 h. Extraction of the cooled solution with ether afforded bicyclohexyl-2,2'-dione (0.55 g), and extraction of the acidified aqueous phase with chloroform provided a residue (0.1 g) from which crystalline dodec-6-enedioic acid was isolated.

(c) *Photolysis*. The peroxide (3.0 g) in methanol (220 cm³) containing Rose Bengal was irradiated for 3 h in a quartz Hanovia photoreactor with a mercury vapour lamp. The solution was evaporated and the residue (2.8 g; acid equiv., 257.3), after methylation (diazomethane), was shown, by g.l.c.—mass spectroscopy, g.l.c.—i.r. spectroscopy, and preparative g.l.c. followed by i.r. and n.m.r. examination, to contain bicyclohexyl-2,2'-dione (1.7%), (\pm)- and *meso*-isomers of the methyl ester of the keto-acid (XI) (3.1%), a component (*ca.* 70%) comprising a mixture of dimethyl dodec-6-enedioate (mainly) and isomeric cyclic diesters, and the dimethyl esters of the isomeric branched-chain acyclic acids [including (XIV)] [ν_{\max} (vapour) 1645 (C=C) and 1755 cm⁻¹ (C=O); ν_{\max} (film) 1640 (C=C) and 1735 cm⁻¹ (C=O); δ_{H} (CCl₄) 1.1—1.9 (complex, CH₂), 2.0—2.4 (complex, CH₂ and CH α to C=C or C=O), 3.58 (s, OMe), and 4.7—5.6 (complex,

⁵ B. W. Baker, R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1954, 1804.

CH=CH₂); *m/e* 256 (*M*) and 234 (*M* - CH₃OH)]. Part (1.05 g) of a similar product of photolysis, after hydrogenation (Adams catalyst) at 20–50° for 3 h, gave a residue (0.9 g), which, by g.l.c.–mass spectroscopy, was found to contain dimethyl adipate (0.5%), dimethyl dodecanedioate (35.8%) [*m/e* 258 (*M*, 0.5%), 227 (42.6), 185 (49.2), and 98 (100.0)], dimethyl 2-*n*-butyloctanedioate (26.6%), and two isomeric diesters (C₁₄H₂₄O₄) (6.9 and 18.9%), probably cyclic [*m/e* 256 (*M*), 224 (*M* - CH₃OH), and 81].

(d) *Pyrolysis*. A solution of the peroxide (3.0 g) in dioxan (30 cm³) was slowly dropped into a heated tube, packed with glass beads, at 400° and 150 mmHg. Removal of the solvent left a residue (2.8 g) from which crystalline dodec-6-enedioic acid (1.55 g) was isolated. Distillation of the filtrate gave material (0.55 g), b.p. 110–130° at 15 mmHg, found, by i.r. and mass spectroscopy, to contain bicyclohexyl-2,2'-dione and octahydrodibenzofuran.

(e) *With formic acid*. (i) The peroxide (5 g) was added to formic acid (20 cm³) below 20°; no active oxygen remained after 1.5 h at 0–20°. The solution was neutralised with sodium hydrogen carbonate solution and extracted with chloroform. Evaporation of the extract left a residue, which, on trituration with ether–petroleum, provided a slightly sticky solid (3.3 g) from which was obtained 3-(2-oxocyclohexyl)oxacycloheptan-2-one (XVI), m.p. 73–76° (from methanol) (Found: C, 68.55; H, 8.6. C₁₂H₁₈O₃ requires C, 68.6; H, 8.6%); ν_{\max} (KBr) 1700 (C=O, ketone) and 1725 cm⁻¹ (C=O, lactone); *m/e* 210 (*M*, 27.5%), 192 (27.5), 150 (C₉H₁₀O₂, 34.8), 114 (C₈H₁₀O₂, McLafferty rearrangement ion, 100.0), and 98 (C₆H₁₀O, McLafferty rearrangement ion, 33.3). Distillation of the mother liquors gave fractions (total 2.0 g) shown by i.r. and mass spectroscopy to contain the keto-lactone (XVI), bicyclohexyl-2,2'-dione, and cyclohexenylcyclohexanone.

(ii) The peroxide (3 g) and formic acid (10 cm³) were heated together on a water-bath for 10 min, and the product was distilled at 15 mmHg to give, in addition to formic acid, fractions (i) (1.2 g), b.p. 210–240°, and (ii) (1.6 g), b.p. 240–250°, and a residue (0.1 g). Fraction (i) contained mainly the keto-lactone (XVI), with additional components which were probably the lactones (XVII) and (XVIII) [ν_{\max} (film) 1675 (C=C), 1720 (C=O), and 3440 cm⁻¹ (OH); δ_{H} (CDCl₃) 2.2 (CH₂-C=C) and 8.05 (s, HCO); *m/e* 238

(C₁₃H₁₈O₄) and 220 (C₁₃H₁₆O₃)]]; fraction (ii) contained the same compounds in different proportions.

*Reaction of Bicyclohexyl-2,2'-dione with *t*-Butyl Hydroperoxide*.—The diketone concentrate (14 g) and 70% *t*-butyl hydroperoxide (30 g) were mixed and stored over solid calcium chloride for 6 days. The mixture was then diluted with ether and filtered, the filtrate was evaporated, and the residue was held at <50° and 1 mmHg. The final residue (24.3 g; peroxide equiv., 193.4) afforded 4a,6a-bis-*t*-butylperoxyperhydrodibenzofuran (VI) (11.6 g), m.p. 51–52° (from ethanol) (Found: C, 67.35; H, 10.5%; peroxide equiv., 186.0. C₂₀H₃₆O₅ requires C, 67.4; H, 10.1%; peroxide equiv., 175); ν_{\max} (KBr) 1000–1200 cm⁻¹ (several bands, O-C-O); δ_{H} (CDCl₃) 1.23 (18H, s, Bu^t) and 1.3–2.6 (18H, complex, CH and CH₂); δ_{C} (CDCl₃) 20.5, 22.6, 23.3, 26.8 (CH₃), 32.4, 38.5, 79.2 (C-O), and 109.5 (O-C-O); *m/e* 355 (*M* - H, 0.1%), 267 (C₁₆H₂₇O₃, 4.5), 98 (10.7), and 73 (C₄H₉O, 100.0).

Reactions of the Peroxide (VI).—(a) *With iron(II) sulphate*. The dioxan (3 g) in dioxan (10 cm³) was warmed with iron(II) sulphate (4 g) in water (10 cm³) at 70° for 4 h. The cooled solution was acidified and extracted with ether. The product (1.6 g) consisted largely of bicyclohexyl-2,2'-dione with some lactones (i.r.).

(b) *Photolysis*. The peroxide (4 g) in petroleum (230 cm³) was irradiated in the quartz Hanovia photoreactor for 1.75 h at room temperature. Evaporation of the solution and distillation of the residue at 15 mmHg gave fractions (i) (1.0 g), b.p. 190–220°, and (ii) (0.9 g), b.p. 220–255°, and a residue (0.3 g). These fractions were shown, by i.r. and mass spectroscopy, to contain bicyclohexyl-2,2'-dione, acids, the anhydride (XIX) (C₁₂H₁₈O₃), and high molecular weight hydrocarbons.

Thermal decomposition of the peroxide at 180–200° gave similar products.

We thank Mr. A. J. Plomer for experimental assistance, Dr. D. L. Gerrard for i.r. spectra, Dr. H. Pyszora for ¹H n.m.r. spectra, Dr. S. A. Knight for ¹³C n.m.r. spectra, Mr. D. F. Francis for g.l.c. analyses, and Mr. D. C. White for elemental analyses. Permission to publish this paper has been given by The British Petroleum Company Ltd.

[4/1534 Received, 24th July, 1974]