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PEROXIDES OF HIGHER ALIPHATIC ETHERS

I. BELIČ,† T. KASTELIC-SUHADOLC,*† R. KAVČIČ,‡ J. MARSEL,‡
V. KRAMER§ and B. KRALJ§
University of Ljubljana, 6100 Ljubljana, Yugoslavia.

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Abstract—The oxidation of higher aliphatic ethers with oxygen at 50° yields two peroxides as the main oxidation products for each ether, namely a dihydroperoxy-dialkyl ether and a dihydroperoxy-dialkyl peroxide. The mass spectra of these compounds are recorded and the main fragmentation pattern is discussed.

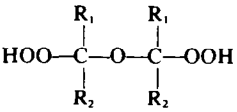
During an investigation of the products of ozonation of tetramethylethylene,[1] peroxides were found which contained, besides the hydroperoxy group, also an ether group. It was desirable to have for comparison some suitable simple peroxides containing both the hydroperoxy and ether groups. Such a compound, 2,2'-dihydroperoxy-2,2'-diisopropyl ether (**1**) was originally prepared by Ivanov, Savinova and Mihajlova.[2] When peroxide **1**, prepared according to Ivanov *et al.*, was analysed by the paper chromatographic method of Milas and Belič,[3] and the TLC method of Buzlanova *et al.*,[4] in addition to H_2O_2 two peroxidic spots were detected. Belič and Suhadolc[5] isolated these two peroxides by preparative TLC and identified them as 2,2'-dihydroperoxy-2,2'-diisopropyl ether (**1**) and 2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (**2**). But the analytical data of the above peroxides, although indicating the proposed structures, did not agree too well with the calculated data. Attempts to improve the analytical data failed because the peroxides were found to be too unstable. The recovery of the active oxygen content on one TLC run was only 60%.

Therefore we wanted to confirm these results by studying the peroxides of higher aliphatic ethers with corresponding structures. It is well known that the replacement of a Me group with Et or Pr groups in a peroxide gives much more stable peroxides. We prepared the peroxides of di-3-pentyl, di-2-pentyl and di-4-heptyl ether[6] by oxidation of the ethers with molecular oxygen. By TLC and PC analysis, we detected two peroxides as the main products in the oxidation mixture of each ether.

With the aid of preparative TLC, both peroxides of di-3-pentyl ether were isolated in a pure state and the purity of both checked by TLC. The peroxide with the higher R_f value, suspected on the basis of its molecular weight, active oxygen content and mass spectrum, to be 3,3'-dihydroperoxy-3,3'-dipentyl peroxide (**6**), was found to have an IR spectrum, mass spectrum and R_f values which were all identical with those of **6** prepared according to Milas and Golubović[7] from 3-pentanone. The peroxide with the lower R_f was identified as 3,3'-dihydroperoxy-3,3'-dipentyl ether (**3**). It had the expected molecular weight, active oxygen content, IR and mass spectrum and solidified when kept for a few weeks at room temperature. This solid peroxide was identified as 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane (**10**) by comparison of its melting point, R_f value and mass spectrum with the authentic sample synthesized according to a known method.[7] Peroxide **6** remained unchanged under the same conditions. It is known that only peroxides containing an ether group rearrange spontaneously, whereas peroxides containing peroxy groups do so only in the presence of strong acids.[1]

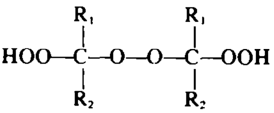
The peroxides of di-2-pentyl ether were isolated by TLC. The peroxide with the higher R_f value was identified as 2,2'-dihydroperoxy-2,2'-dipenthyl peroxide (**7**) but the peroxide with the lower R_f as 2,2'-dihydroperoxy-2,2'-dipentyl ether (**4**). The ether **4** transformed after standing for a few weeks at room temperature into 3,6,9-trimethyl-3,6,9-tripropyl-1,2,4,5,7,8-hexaoxacyclononane (**11**). Peroxide **7** remained unchanged under the same conditions.

The peroxides of di-4-heptyl ether were analysed by TLC. The peroxide with the higher R_f value was identified as 4,4'-dihydroperoxy-4,4'-diheptyl peroxide (**9**) and the peroxide with the lower R_f value as 4,4'-dihydroperoxy-4,4'-diheptyl ether (**5**).



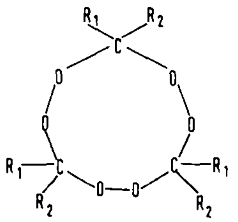
$$\mathrm{HOO{-}\overset{R_1}{\underset{R_2}{C}}{-}O{-}\overset{R_1}{\underset{R_2}{C}}{-}OOH}$$

1: $R_1 = R_2 = CH_3$
3: $R_1 = R_2 = C_2H_5$
4: $R_1 = CH_3$
$R_2 = CH_2CH_2CH_3$
5: $R_1 = R_2 = CH_2CH_2CH_3$



$$\mathrm{HOO{-}\overset{R_1}{\underset{R_2}{C}}{-}O{-}O{-}\overset{R_1}{\underset{R_2}{C}}{-}OOH}$$

2: $R_1 = R_2 = CH_3$
6: $R_1 = R_2 = C_2H_5$
7: $R_1 = CH_3$
$R_2 = CH_2CH_2CH_3$
8: $R_1 = CH_3$
$R_2 = CH(CH_3)_2$
9: $R_1 = R_2 = CH_2CH_2CH_3$



10: $R_1 = R_2 = C_2H_5$
11: $R_1 = CH_3$
$R_2 = CH_2CH_2CH_3$
12: $R_1 = CH_3$
$R_2 = CH(CH_3)_2$

Peroxides **8** and **12** were prepared only for the comparison of mass spectra.

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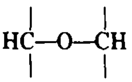
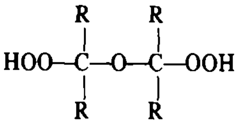
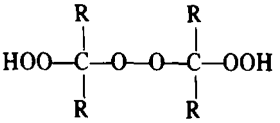
*Taken in part from the doctoral thesis of T. Kastelic-Suhadolc.
†Biochemical Institute of the Medical Faculty.
‡Department of Chemistry.
§"J. Stefan" Institute.

Our investigation shows that oxidation of aliphatic ethers with a  $\overset{|}{\underset{|}{\mathrm{HC}}}\mathrm{-O-}\overset{|}{\underset{|}{\mathrm{CH}}}$ group gives as the main product a mixture of dihydroperoxy-dialkyl ethers  $\mathrm{HOO-}\overset{R}{\underset{R}{\mathrm{C}}}\mathrm{-O-}\overset{R}{\underset{R}{\mathrm{C}}}\mathrm{-OOH}$ and dihydroperoxy-dialkyl peroxides  $\mathrm{HOO-}\overset{R}{\underset{R}{\mathrm{C}}}\mathrm{-O-O-}\overset{R}{\underset{R}{\mathrm{C}}}\mathrm{-OOH}$ and not only dihydroperoxy-dialkyl ethers as believed earlier.[2]

The mass spectra. The analysis and structure elucidation of organic peroxides can cause serious problems in most instances. Because of the thermal instability of many organic peroxides, they are generally considered as unsuitable for treatment by mass spectrometry. However, as will be shown, much usable information of analytical importance can be drawn from their mass spectra.

There have been a few papers on the mass spectral investigation of organic peroxides,[8-11] but none concerning the behaviour of dihydroperoxy-dialkyl ethers and related peroxides.

The compounds under investigation are very sensitive to temperature rise, as well as to electron impact. Their mass spectra (Table 1) show no molecular ions at all (**3** and **4**) or they are of very low abundance (**5**–**12**). But, on the other hand, they form many intense fragment ions which are characteristic of this type of structure and therefore usable for identification purposes. Many fragment ions are compositionally common to all compounds or at least within a series of isomers.

The mass spectra of compounds **3**–**12** are listed in Table 1. Besides M^+, only those ions are given beyond *m/e* 42 having intensities greater than 1% of the base peak.

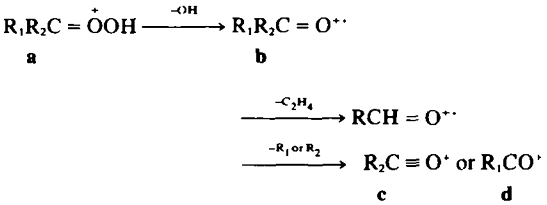
Dihydroperoxy-dialkyl ethers. Both isomers, i.e. **3** and **4**, having molecular weights 222, decompose under electron impact ionization giving fragment ions of highest mass *m/e* 103. These ions (designated by **a** in Scheme 1) can only be formed by cleavage of a C–O ether bond. The elimination of an OH radical from **a** gives rise to the ion *m/e* 86 (**b**), which decomposes further by two routes, i.e.

Table 1. Principal ions in the mass spectra of compounds 3–12

m/e	3	4	5	6	7	8	9	10	11	12
43	19	100	100	1	72	100	100	8	100	100
44	15	5	11	-	3	5	5	9	5	3
45	-	16	22	-	6	5	2	40	8	1
55	-	-	51	-	-	-	-	-	-	-
56	-	-	21	5	-	-	-	21	-	-
57	100	8	41	81	-	-	1	100	7	-
58	27	20	11	3	17	-	3	28	35	-
61	-	3	-	-	2	-	-	-	12	-
69	-	-	21	-	-	-	-	9	-	-
70	-	-	22	-	-	-	-	-	-	-
71	-	35	62	-	27	13	63	-	38	11
73	-	-	42	-	-	-	-	-	-	-
74	3	-	-	5	13	-	-	-	-	-
75	-	-	-	2	-	-	-	81	-	-
77	-	-	-	-	21	12	-	-	-	-
86	29	42	3	38	33	28	-	22	19	6
87	11	12	-	22	28	12	-	61	31	24
91	-	-	-	39	-	-	-	-	-	-
103	17	87	-	100	100	42	-	32	5	-
104	-	8	-	6	6	-	-	-	-	-
105	-	-	-	-	-	-	17	-	-	-
113	-	-	13	-	-	-	-	-	-	-
114	13	2	-	-	-	-	18	-	-	-
115	-	-	-	-	-	-	12	1	-	-
119	-	-	-	8	28	1	-	-	-	-
131	-	-	-	-	-	-	27	-	-	-
147	-	-	-	-	-	-	1	-	-	-
238	-	-	-	0.3	0.4	0.1	-	-	-	-
278	-	-	0.02	-	-	-	-	-	-	-
294	-	-	-	-	-	-	0.02	-	-	-
306	-	-	-	-	-	-	-	0.05	0.06	0.02

isomer **3** eliminates either C_2H_4 or the C_2H_5 radical forming ions *m/e* 58 and the base peak at *m/e* 57 (**c**), respectively. The decomposition of isomeric ion **b** in **4** takes place in a similar way where alternatively C_2H_4, CH_3 or C_3H_7 are lost. The ions formed at *m/e* 71 and 43 (base peak) allow an unambiguous differentiation between **3** and **4**. Of course the positive charge is also well stabilized on the propyl ion, having an identical nominal mass to CH_3CO^+, i.e. 43. It seems that the propyl ion most likely arises from **a** or even directly from the molecular ion, but the respective pathways were not tested.

Thus, by analogy, the fragmentation pattern of **3** and **4** seems similar to that found in alkyl ethers and alcohols.[12] Compared with alcohols, the OOH group weakens the adjacent C–O bond to a greater extent, decreasing the stability of molecular ions. Extension of alkyl chains in **5** reduces this electron withdrawing effect slightly, making possible the formation of a molecular ion peak of low intensity at 278. Other prominent ions formed in **5** are identical to those in **4**, e.g. *m/e* 43 ($C_3H_7^-$), *m/e* 71 ($C_3H_7CO^+$).



$$\underset{\mathbf{a}}{R_1R_2C=\overset{+}{O}OH} \xrightarrow{-OH} \underset{\mathbf{b}}{R_1R_2C=O^{+\cdot}}$$

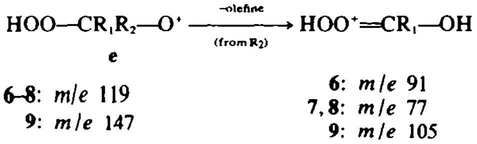
$$\xrightarrow{-C_2H_4} RCH=O^{+\cdot}$$

$$\xrightarrow{-R_1\text{ or }R_2} \underset{\mathbf{c}}{R_2C\equiv O^+}\text{ or }\underset{\mathbf{d}}{R_1CO^+}$$

Scheme 1.

Dihydroperoxy-dialkyl peroxides. In distinction to ethers **3** and **4**, the corresponding peroxides **6** and **7** exhibit well detectable M^+ ions. In isomer **8** the M^+ ion appears with the same order of magnitude. The compound **9** exhibits a molecular ion which is only about one tenth as intense of those in **6–8**. In general, the mass spectra of isomers **6–8**, as well as **9**, show many common features. Their molecular ions decompose by cleavage of the peroxide O–O bond. The ions formed (ions **e**, Scheme 2) represent half of the original molecules and are of moderate intensities. Starting from M^+, a further significant fission occurs giving rise to very abundant ions of type **a** (*m/e* 103 at **6–8** and *m/e* 131 in **9**). In this respect the cleavage is quite identical to that found in ethers **3** and **4**.

The lower part of the spectra is dominated by intense alkyl ions most likely formed directly from molecular ions, i.e. *m/e* 29 (C_2H_5), 43 ($CH_2CH_2CH_3$) in **7** and **9**, and $CH(CH_3)_2$ in **8**, or also from secondary fragmentations of ions **a** and **e**. It is evident that these processes cannot be distinguished quantitatively.



$$\underset{\mathbf{e}}{HOO-CR_1R_2-O^\cdot} \xrightarrow[\text{(from }R_2)]{-\text{olefine}} HOO^+=CR_1-OH$$

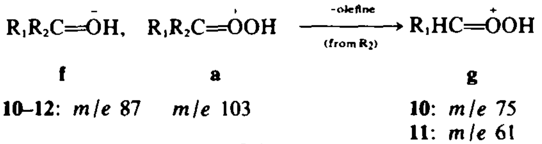
6–8: *m/e* 119
9: *m/e* 147

6: *m/e* 91
7, 8: *m/e* 77
9: *m/e* 105

Scheme 2.

Molecular ions can also eliminate a HOO-radical to form ions *m/e* 205 in **6–8** and *m/e* 261 in **9** whose relative intensities are below 0.5% and therefore not shown in Table 1. This process was observed earlier in simple alkyl hydroperoxides.[9] As might be expected, ions **e** should also lose HOO˙ to form ions **b**, i.e. *m/e* 86 in **6–8** and 131 in **9**. But it was impossible to confirm this pathway by the transition of metastable ions. Thus we consider that the ions **b** originate mainly from **a**, whose decomposition is accompanied by a metastable transition detected in the first field free region of a double focusing mass spectrometer. Further decomposition of ions **b**, losing alternatively one of the alkyl groups, points to the ions of type **c** and **d**. In contradistinction to ethers **3** and **4**, the olefine elimination (C_2H_4 or C_3H_6) takes place in **6–9** not from ions **b** but **e** (Scheme 2). The presence of peaks **b** + H (*m/e* 87 in **6–8** and *m/e* 115 in **9**) suggests that the fragmentation of $M^{+\cdot}$ is accompanied by a hydrogen migration from the departing radical to the carbonium ion (**a** + H). The last ion then decomposes giving rise to **b** + H. An identical pathway is assumed in **3** and **4** where ions *m/e* 87 also occur.

Cyclic peroxides. The stability of $M^{+\cdot}$ ions in compounds **10**, **11** and **12** is still lower than in **6–9**. The most intense ions in their spectra are alkyl ions, i.e. *m/e* 29 in **10** and *m/e* 43 in **11** and **12**. At first glance it seems a little unexpected that so many identical ions to those described above can also be generated from cyclic structures. However, **10** and **11** exhibit ions of types **a**, **b** and **c** or **d**. Also ions **b** + H (designated by **f** in Scheme 3) are present in all three spectra. Moreover, their abundances greatly exceed those of ions **b**.



$$\underset{\mathbf{f}}{R_1R_2C=\overset{-}{O}H},\quad \underset{\mathbf{a}}{R_1R_2C=\overset{+}{O}OH} \xrightarrow[\text{(from }R_2)]{-\text{olefine}} \underset{\mathbf{g}}{R_1HC=\overset{+}{O}OH}$$

10–12: *m/e* 87
m/e 103
10: *m/e* 75
11: *m/e* 61

Scheme 3.

The ions **f** can only be formed from $M^{+\cdot}$, whereas **g** originate most probably from ions **a** expelling C_2H_4 (**10**) or C_3H_6 (**11**). Regarding ions **a**, the fragmentation behaviour of **11** and **12** deviate somewhat from that in **10**. We suppose that the favoured formation of the isopropyl ion (*m/e* 43) in **12**, and to lesser extent also the formation of the propyl ion in **11**, hinders the generation of ion **a**. Therefore, also ions of type **b**, **c** and **g**, derived from **a** in **12**, are of minor intensities.

In conclusion, although here the $M^{+\cdot}$ ion peaks are hardly detectable or even absent, it can be seen from the interpretation outlined above that many characteristic features in these spectra allow confirmation of a particular compound. Thus the dihydroperoxy-dialkyl ethers decompose giving ions of type **a** but no ions **e** were found at all. On the other hand, the related peroxides form, besides **a**, also an appreciable amount of ions **e**. In cyclic peroxides the abundances of ions $R_1R_2 = OH^+$ (**f**) always exceed those of ions $R_1R_2C = O^{+\cdot}$ (**b**), which in turn are more pronounced in all other peroxides listed above. Thus, in spite of experimental difficulties encountered in mass spectrometric identification of organic peroxides, the basic information gained makes mass spectrometry the method of choice.

EXPERIMENTAL

The mass spectra were obtained on a CEC-21-110C instrument at 70 eV, 150 μA ionizing current and 6 kV accelerating voltage. Sample introduction was performed by a direct inlet system which allows the use of "melting point" capillary tubes. To reduce the vapour pressure to the desired value and to avoid an excessive thermal decomposition in the ion source, some precautions were taken. The peroxide was placed in a capillary tube which was then drawn out to a narrow neck using a very small flame. To avoid explosion of the peroxide the sample was frozen with liquid nitrogen. The whole length of the capillary was about 3 cm and suitable for placing in the introduction rod. The ion source block was cooled down to 0–10° by means of a "thermal conducting device" consisting of a copper strip, one end of which was connected to the ion source block, while the other end was cooled by liquid nitrogen from outside the source. To achieve the appropriate sample pressure, only a heater around the sample holder was used. The only disadvantage is that the ion source had to be baked out before a new sample was introduced.

NMR spectra were obtained with a JEOL PS-100 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane as 0 ppm (δ scale). NMR spectra were obtained in $CDCl_3$. IR spectra were determined with Perkin–Elmer 25 and 180 spectrometers. TLC analyses were performed with a mixture of toluene–methanol (20:4 vol/vol) on silica gel G thin layer plates. Peroxides were visualized according to Knappe and Peteri[13] by a methanolic soln of N,N′-dimethyl *p*-phenylene-diamine dihydrochloride. Paper chromatographic analyses[3] were made with decalin saturated with dimethyl formamide on Whatman 1 paper.

Oxidations. The oxidation of aliphatic ethers was carried out with O_2 in the presence of an external light source (SEG high-pressure lamp, 550 W) at the temp. of 50°. The preparation of the appropriate ethers was reported earlier.[6] A cylindrical quartz glass reactor (200 × 20 mm), equipped with a gas-dispersing tube and a reflux condenser was used for the oxidations of 36.5 g of di-3-pentyl ether and 22 g of di-2-pentyl ether. Cylinder O_2 was the oxidant. The progress of the oxidation was followed by withdrawal of samples at arbitrary time intervals and immediate analysis of these samples for hydroperoxide by the iodometric method.[14] The maximum concentration of the hydroperoxide of di-3-pentyl ether was reached in 13 hr oxidation and that of di-2-pentyl ether in 9 hr. A cylindrical quartz glass reactor (160 × 16 mm) was used for the oxidation of 15 g of di-4-heptyl ether. The maximum concentration of hydroperoxide of di-4-heptyl ether was reached in 6 hr.

The oxidation mixture of di-3-pentyl ether when analysed by TLC gave intense spots with R_f 0.17, 0.87 and 0.0 (H_2O_2) and two faint spots with R_f 0.40 and 0.57. Di-3-pentyl ether was distilled from the oxidation mixture at a pressure of 3 mm Hg and a temp. of 30–31°.

3,3′-*Dihydroperoxy*-3,3′-*dipentyl ether* (**3**). R_f 0.17, IR spectrum (νOH) 3420, (νCH) 2970, 2940, 2880, 2840, (δCH) 1453, 1440, 1375, (δOOH) 1340, (νCO) 1150, (νOO) 910, (δ dihedral angle) 850 cm^{-1}; Found: (O), 13.30%, mol. wt. 223 (exaltone); $C_{10}H_{22}O_5$, requires: (O), 14.40%, mol. wt. 222.15.

3,3′-*Dihydroperoxy*-3,3′-*dipentyl peroxide* (**6**). R_f 0.87, IR spectrum (νOH) 3410, (νCH) 2975, 2940, 2880, (δCH) 1460, 1443, 1380, (δOOH) 1347, (νCO) 1150, (νOO) 918, (δ dihedral angle) 856 cm^{-1}; Found: (O), 20.6%, mol. wt. 232 (exaltone); $C_{10}H_{22}O_6$ requires: (O), 20.16%, mol. wt. 238.14. Analysis of **3** and **6** by the paper chromatographic method of Milas and Belič[3] gave spots with R_f 0.05 and 1.00, respectively.

The oxidation mixture of di-2-pentyl ether, analysed by TLC, gave intense spots with R_f 0.16, 0.85 and 0.0 (H_2O_2) besides two faint spots with R_f 0.36 and 0.65. Di-2-pentyl ether was distilled from the oxidation mixture at 3 mm of Hg at a temp. of 30–31°.

2,2′-*Dihydroperoxy*-2,2′-*dipentyl ether* (**4**). R_f 0.16; Found: (O), 13.5%, mol. wt. 220 (exaltone); $C_{10}H_{22}O_5$ requires: (O), 14.40%, mol. wt. 222.15. The ether **4** tranformed into **11**. The m.p. and R_f value of **11** and authentic peroxide synthesized according to the method for 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane,[7] were identical. The product gained was recrystallized several times at −70° from MeOH, m.p. 38–40°. TLC showed a single spot with R_f 0.90.

2,2′-*Dihydroperoxy*-2,2′-*dipentylperoxide* (**7**). R_f 0.85; Found: (O), 20.5%, mol. wt. 234 (exaltone); $C_{10}H_{22}O_6$ requires: (O), 20.16%, mol. wt. 238.14. Paper chromatographic analysis of **4** and **7** gave spots with R_f 0.04 and 0.81, respectively.

The R_f values obtained by TLC and PC and the mass spectrum of **7** were identical with those of authentic 2,2′-dihydroperoxy-2,2′-dipentyl peroxide prepared according to the following procedure: 6.8 g (0.1 mol) of 50% H_2O_2, cooled to −5°, was stirred while 2.4 g (0.025 mol) of conc H_2SO_4 was added. To this stirred soln 8.6 g (0.1 mol) of methyl-propyl ketone was added dropwise in the course of 1 hr. Stirring was continued at −5° to 0° for 4 hr, then the mixture was extracted with pentane, the extract washed with satd ammonium sulfate soln, then with water, and dried over $MgSO_4$. The soln was filtered, concentrated *in vacuo* and cooled at −70°. The colourless crystals which separated were recrystallized eight times at −70° from pentane, m.p. 33–34.5°. IR spectrum: (νOH) 3410, (νCH) 3000, 2960, 2930, 2875, (δCH) 1465, 1455, (δOOH) 1370, (νCO) 1170–1137, (νOO) 940, (δ dihedral angle) 840 cm^{-1}. NMR spectrum: δ9.27, s, 1H: (OOH); 1.60–1.80, m, 4H: (CH_2); 1.40, s, 3H: ($C{-}CH_3$); 0.91, t, 3H: ($CH_2{-}CH_3$). Found: (O), 20.3, $C_{10}H_{22}O_6$ requires: (O), 20.16%.

The oxidation mixture of di-4-heptyl ether analysed by TLC gave intense spots with R_f 0.52, 0.84 and 0.0 (H_2O_2), besides two faint spots with R_f 0.33 and 0.63. The peroxides in the oxidation mixture were separated by column chromatography on silica gel, eluted with benzene (19 × 10 ml fractions) and further with a mixture of benzene–methanol (100:5 vol/vol). The fractions from 7 to 9 contained peroxide with R_f 0.84 and fractions from 11 to 24 peroxide with R_f 0.52.

4,4′-*Dihydroperoxy*-4,4′-*diheptyl ether* (**5**). R_f 0.52, IR spectrum (νOH) 3400, (νCH) 2960–2875, (δCH) 1450, 1372, (δOOH) 1330, (νCO) 1157–1100, (νOO) 900, (δ dihedral angle) 845 cm^{-1}. Found: (O) 11.8%, mol. wt. 275 (exaltone); $C_{14}H_{30}O_5$ requires: (O) 11.50%, mol. wt. 278.21.

4,4′-*Dihydroperoxy*-4,4′-*diheptyl peroxide* (**9**). R_f 0.84, IR spectrum (νOH) 3382, (νCH) 2980–2870, (δCH) 1460, 1370, (δOOH) 1330, (νCO) 1155–1133, (νOO) 870, (δ dihedral angle) 850 cm^{-1}. Found: (O) 16.0%, mol.wt. 300 (exaltone); $C_{14}H_{30}O_6$ requires: (O), 16.31%, mol. wt. 294.20. The R_f values obtained by TLC and PC, the mass spectrum and IR spectrum of this peroxide were identical with those of the 4,4′-dihydroperoxy-4,4′-diheptyl peroxide synthesized according to the method for **6**. The colourless crystals obtained were recrystallized several times at −30° from pentane. M.p. 54°C. NMR spectrum: δ9.84, s, 1H: (OOH); 1.2–1.8, m, 8H: ($CH_2{-}CH_2$); 0.96, t, 3H: ($C{-}CH_3$).

2,2′-*Dihydroperoxy*-2,2′-*diisopentyl peroxide* (**8**) was synthesized as peroxide **6**. The soln of **8** in pentane was cooled to −40°. The colourless crystals were recrystallized several times (first at −20°, then at 0°) from pentane, m.p. 90–91° (lit.[15] 90.5–91°). The yield was 40%. TLC showed a single spot with R_f 0.84. IR spectrum (νOH) 3422, (νCH) 2980, (δCH) 1460, 1440, (δOOH) 1383, 1367, (νCO) 1130, (νOO) 920, (δ dihedral angle) 846 cm^{-1}. NMR spectrum: δ 9.60, s, 1H: (OOH); 2.32, m, 1H: (CH of isopropyl group); 1.38, s, 3H: ($C{-}CH_3$); 1.0, d, 6H: (CH_3 of isopropyl group).

3,6,9 - *Trimethyl* - 3,6,9 - *triisopropyl* - 1,2,4,5,7,8 - *hexaoxacyclononane* (**12**) was synthesized according to the modified method of Wulz and Brune.[15] To a stirred soln of 12 g of 30% H_2O_2, 10 g of conc H_2SO_4 and 15 g of Ac_2O cooled to about −15°, a soln of 10 g of methyl-isopropyl ketone in 5 ml of conc AcOH was added slowly. The mixture was allowed to stand one month at 0° and then extracted with pentane. The extract was washed and dried as in the above procedure. The soln was filtered, concentrated and cooled to −40°. The colourless crystals which separated were recrystallized several times from pentane and MeOH, m.p. 60.5–61°. The yield was 11%. TLC analysis showed a single spot with R_f 0.91. IR spectrum (νCH) 2980, 2945, 2880, (δCH) 1464, 1440, (νOO) 920 (δ dihedral angle) 860 cm^{-1}.

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