Synthesis of peroxide compounds by the BF_3-catalyzed reaction of acetals and enol ethers with H_2O_2*

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Aliphatic and alicyclic *gem*-bis-hydroperoxides and their derivatives, bis(1-hydroperoxycycloalkyl) and bis(1-hydroperoxyalkyl) peroxides, dispiro- and tetraalkyl-1,2,4,5-tetroxanes were synthesized by the reaction of aliphatic and alicyclic acetals and enol ethers with H_2O_2 in the presence of BF_3 in anhydrous Et_2O.

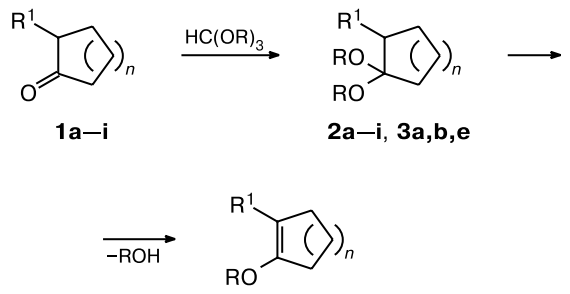
Key words: acetals, enol ethers, boron trifluoride complexes with Et_2O and MeOH, *gem*-bis-hydroperoxides, bis(1-hydroperoxycycloalkyl) and bis(1-hydroperoxyalkyl) peroxides, dispiro- and tetraalkyl-1,2,4,5-tetroxanes.

In recent years, the enhanced interest of chemists arose in organic bis-hydroperoxides and 1,2,4,5-tetroxanes related to the high pharmacological activity of the latter, in particular, an antimalarial activity.[2—9]

Bis-hydroperoxides are usually prepared by ozonization of enol ethers or α-olefins in the presence of H_2O_2,[7—10] by the reaction of H_2O_2 with ketones in HCO_2H, $EtCO_2H$, MeCN, and other solvents,[7—11] and by hydroperoxidation of acetals catalyzed by tungstic acid.[12] None of these methods complies with the up-to-date requirements due to the low or moderate yields of the target products, experimental complexity, and long process durations. In addition, the selectivity of ozonization is low and its use is limited to enol ethers and olefins that contain no other groups sensitive to ozone. Therefore, studies directed at the development of more perfect approaches to organic *gem*-bis-hydroperoxides remain topical.

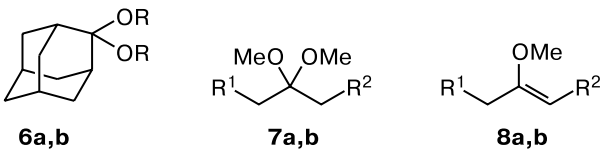
Here we report two new methods for the synthesis of bis-hydroperoxides and their derivatives, *viz.*, bis(1-hydroperoxycycloalkyl) and bis(1-hydroperoxyalkyl) peroxides and dispiro- and tetraalkyl-1,2,4,5-tetroxanes, which allow one to prepare these compounds simpler, faster, and in higher (or comparable) yields (70—95%) than the methods described previously.[7—12] The methods are based on reactions of acetals and enol ethers with H_2O_2 in anhydrous ether catalyzed by BF_3 complexes. We studied these reactions for compounds obtained from the corresponding cycloalkanones **1**, namely, acetals **2** and **3** and enol ethers **4** and **5** (Scheme 1); for acetophenone, α-tetralone, and adamantan-2-one acetals (**6a,b**); 4-methylpetan-2-one (**7a**) and pentadecan-8-one (**7b**) ketals, and enol ethers **8a,b**.

Scheme 1



1—5	a	b	c	d	e	f	g	h	i
n	1	2	3	4	8	1	2	8	8
R^1	H	H	H	H	H	$C_8H_{17}{}^n$	Me	$C_9H_{19}{}^n$	$PhCH_2$

R = Me (**2a—i**, **4b,e,g,h**), Et (**3a,b,e**, **5b,e**)



6a,b **7a,b** **8a,b**

R = Me (**6a**), Et (**6b**); R^1 = H, R^2 = $CHMe_2$ (**7a**, **8a**); $R^1 = R^2 = C_6H_{13}{}^n$ (**7b**, **8b**)

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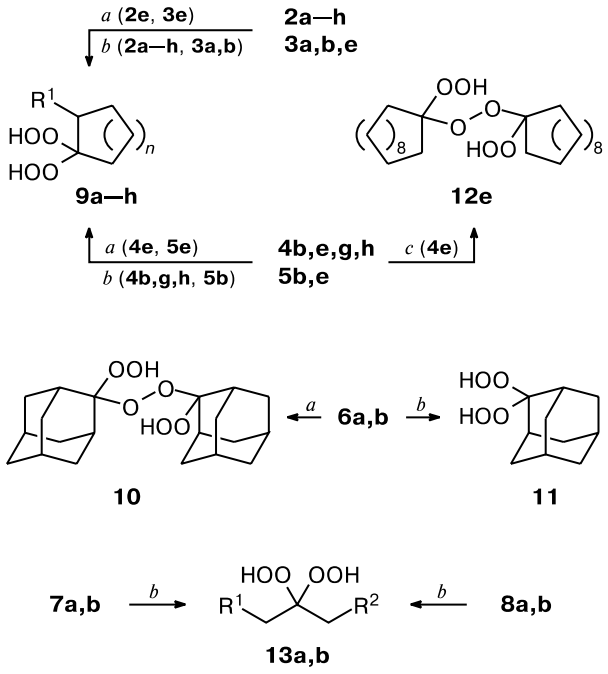
The reactions were carried out at 20 °C, acetals or enol ethers being gradually added to a solution of H_2O_2 in anhydrous diethyl ether containing a catalytic amount (usually 0.1—0.3 equivalents) of $BF_3 \cdot OEt_2$ or $BF_3 \cdot MeOH$. Under these conditions with a 2.5—3-fold molar excess of H_2O_2, ketals and enol ethers obtained from cyclododecanone (**2e**, **3e**, **4e**, **5e**) were selectively converted into (cyclododecylidene)bishydroperoxide (**9e**), adamantan-2-one acetals **6a,b** were transformed into bis(2-hydroperoxyadamantan-2-yl) peroxide (**10**), and ether **4e** gave bis(1-hydroperoxycyclododecyl) peroxide (**12e**) (Scheme 2). Acetals of adamantan-2-one (**6a**), 2-nonylcyclododecanone (**2h**), and 5—8-membered cycloalkanones (**2a—d,f**, **3a,b**) and enol ethers derived from 5—8-membered cycloalkanones (**4b,g**, **5b**), 4-methylpentan-2-one (**8a**), and pentadecan-8-one (**8b**) can selectively be transformed into the corresponding bis(hydroperoxides) (**11**, **9a—d**, **9f—h**, **13a,b**) only in the presence of a 7—8-fold excess of H_2O_2. This approach allowed the preparative-scale synthesis of a dozen of bis-hydroperoxides in yields from 48 to 95% (Tables 1 and 2); almost half of these compounds have not been described previously.

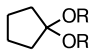
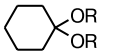
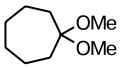
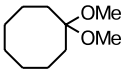
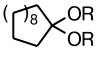
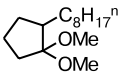
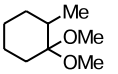
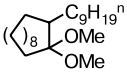
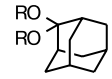
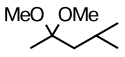
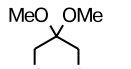
Scheme 2



R^1 = H, R^2 = $CHMe_2$ (**7a**, **8a**, **13a**); R^1 = R^2 = $C_6H_{13}^n$ (**7b**, **8b**, **13b**)

Reagents and conditions: *a*. Et_2O, H_2O_2 (2.5—3 equiv.), $BF_3 \cdot Et_2O$ (MeOH) (0.1—0.3 equiv.), ~20 °C, 1—3 h; *b*. Et_2O, H_2O_2 (7—8 equiv.), $BF_3 \cdot Et_2O$ (0.2—0.4 equiv.), ~20 °C, 1 h; *c*. Et_2O, H_2O_2 (1 equiv.), $BF_3 \cdot Et_2O$ (1 equiv.), ~20 °C, 15 min; (for the indices of compounds **9a—h**, see Scheme 1).

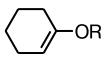
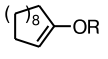
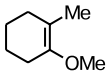
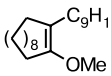
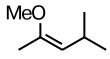
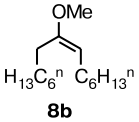
Table 1. Products of $BF_3 \cdot OEt_2$-catalyzed reaction of acetals with H_2O_2[a]

Run	Acetal[b]	Acetal : : H_2O_2	$BF_3 \cdot OEt_2$ /equiv. (method)[c]	Product yield (%)
1	 **2a, 3a**	1 : 2.5	0.2 (*A*)	**9a** (60), **12a** (30—32)
2		1 : 8	0.4 (*B*)	**9a** (79)
3	 **2b, 3b**	1 : 3	0.2 (*A*)	**9b** (62—65), **12b** (25)
4		1 : 2.5	0.2[d] (*A*)	**9b** (61), **12b** (29)
5		1 : 3	0.3 (*A*)	**9b** (30), **12b** (59)
6		1 : 8	0.3 (*B*)	**9b** (86)
7	 **2c**	1 : 7	0.3 (*A*)	**9c** (80)
8	 **2d**	1 : 2.5	0.2 (*B*)	**9d** (9), **12d** (59)
9		1 : 7	0.3 (*B*)	**9d** (71)
10	 **2e, 3e**	1 : 2.5	0.2 (*C*)	**9e** (92—95)
11		1 : 2.5	0.2[d] (*C*)	**9e** (91)
12	 **2f**	1 : 7	0.4 (*B*)	**9f** (77)
13	 **2g**	1 : 1.5	0.2 (*B*)	**9g** (70), **12g** (15), **14g** (6)
14	 **2h**	1 : 3	0.2 (*B*)	**9h** (19), **1h** (70)
15		1 : 8	0.2 (*B*)	**9h** (64)
16	 **6a,b**	1 : 8	0.2 (*B*)	**11** (84)
17		1 : 3	0.15 (*A*)	**10** (64)
18	 **7a**	1 : 2.5	0.3 (*A*)	**12a** (54), **15a** (11)
19		1 : 8	0.2 (*B*)	**12a** (78)
20	 **7b**	1 : 3	0.3 (*A*)	**12b** (44), **15b** (22), **16b** (19)
21		1 : 3	0.4 (*A*)	**12b** (32), **15b** (16), **16b** (27)
22		1 : 8	0.2 (*B*)	**12b** (48)

[a] Et_2O (40—70 mL) as the solvent, ~20 °C, 1—2 h.
[b] R = Me (**2**, **6a**), Et (**3**, **6b**).
[c] Methods *A, B,* and *C* are described in the Experimental.
[d] Catalyzed by $BF_3 \cdot MeOH$.

The reactions of the majority of enol ethers and acetals studied with a less than a seven-fold molar excess of

Table 2. Products of the $BF_3 \cdot OEt_2$-catalyzed reaction of enol ethers (EE) **4**, **5**, and **8** with H_2O_2[a]

Enol ether[b]	EE : H_2O_2	$BF_3 \cdot OEt_2$ /equiv. (method)[c]	Product yield (%)
 **4b, 5b**	1 : 3	0.3 (*A*)	**9b** (49), **12b** (24)
	1 : 3	0.3[d] (*A*)	**9b** (55), **12b** (29)
	1 : 3[e]	0.3 (*B*)	**9b** (55)
	1 : 7	0.2 (*B*)	**9b** (76-83)
 **4e, 5e**	1 : 2.5	0.05 (*C*)	**9e** (71)
	1 : 2.5	0.1 (*C*)	**9e** (86)
	1 : 2.5	0.2 (*C*)	**9e** (89)
	1 : 2.5[e]	0.3 (*C*)	**9e** (79)
	1 : 2.5	0.5 (*C*)	**9e** (93)
	1 : 1	0.6 (*C*)	**9e** (7), **12e** (52)
	1 : 1	1.0 (*A*)	**12e** (50)
	1 : 7	0.3 (*C*)	**9e** (99)
	1 : 3	0.1[f] (*C*)	**9e** (20)
	1 : 3	0.2[g] (*C*)	**9e** (68)
	1 : 3	0.4[d] (*C*)	**9e** (90)
 **4g**	1 : 2.5	0.2 (*A*)	**9g** (71), **12g** (12), **14g** (6)
	1 : 7	0.3 (*B*)	**9g**(79)
 **4h**	1 : 7	0.3 (*B*)	**9h** (64)
 **8a**	1 : 3	0.3 (*A*)	**12a** (73), **15a** (15)
	1 : 2.5	0.3 (*B*)	**15a** (16),
	1 : 8	0.3 (*B*)	**12a** (81), **16a** (44)
 **8b**	1 : 3	0.2 (*A*)	**12b** (55), **15b** (29), **16b** (51)
	1 : 2.5	0.15 (*B*)	**12b** (64)
	1 : 8	0.3 (*B*)	**15b** (8)

[a] Et_2O (40—70 mL) as the solvent, ~20 °C, 0.5—1 h.
[b] R = Me (**4b,e**), Et (**5b,e**).
[c] The variants of the workup of the reaction mixture *A, B,* and *C* are described in the Experimental.
[d] Catalyzed by $BF_3 \cdot MeOH$.
[e] The reaction was carried out at 0 °C.
[f] Catalyzed by H_2SO_4.
[g] Catalyzed by TsOH.

H_2O_2 afforded not only the expected bis-hydroperoxides, but also their derivatives, namely, bis(1-hydroperoxycycloalkyl)- and bis(1-hydroperoxyalkyl) peroxides and dispiro- and tetraalkyl-1,2,4,5-tetroxanes. Indeed, with a 1.5- to 3-fold molar excess of H_2O_2, acetals **2a,b,d**, **3a,b**, and **7a** and enol ether **5b** give rise to bis-hydroperoxides **9a,b,d** and **13a**, bis(hydroperoxycycloalkyl) peroxides **12a,b,d**, and bis(2-hydroperoxy-4-methylpentan-2-yl) peroxide **15a** in an overall yield of 73—92%. In the case of acetals **2g** and **7b** and enol ethers **4g** and **8a,b**, in addition to expected bis-hydroperoxides **9g** and **13a,b**, bis(1-hydroperoxy-2-methylcyclohexyl) peroxide (**12g**), and bis(hydroperoxyalkyl) peroxides **15a,b**, the reactions give dispirotetroxane **14g** and tetraalkyltetroxanes **16a,b** in yields of 6, 44, and 19—51%, respectively (Scheme 3, see Tables 1 and 2).

The ratio of bis-hydroperoxides to their derivatives changes in favor of the latter with an increase in the catalyst concentration (see Table 1, runs *3* and *5*, *20* and *21*), which attests indirectly that the $BF_3 \cdot OEt_2$ and $BF_3 \cdot MeOH$ complexes catalyze both the transformation of acetals and enol ethers into bis-hydroperoxides and the further transformation of bis-hydroperoxides into their derivatives. The experimental proof of this assumption carried out for bis-hydroperoxide **13a** confirmed that $BF_3 \cdot OEt_2$ does actually catalyze its conversion into peroxide **15a** and tetroxane **16a**.

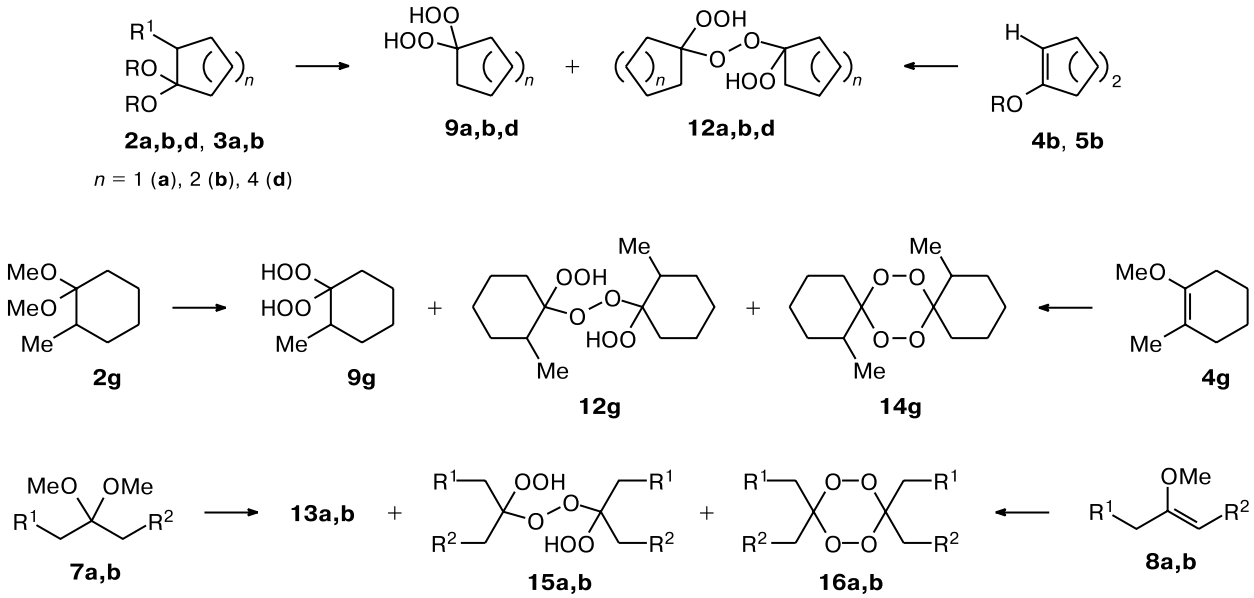
The optimum amount of the catalyst with respect to acetal or enol ether is 0.1—0.2 moles, as shown for hydroperoxidation of acetal **2e** and enol ether **5e**. The $BF_3 \cdot OEt_2$ and $BF_3 \cdot MeOH$ complexes catalyze these reactions with approximately equal efficiencies; the reactions involve apparently the intermediate formation of boron-trifluoride complexes of acetals and H_2O_2 adducts with enol ethers (Scheme 4).

It is noteworthy that the new methods of synthesis of bis-hydroperoxides and their derivatives are inapplicable to acetals and enol ethers obtained from aryl-substituted acetones (acetophenone, α-tetralone, and 2-benzylcyclododecanone (**1i**)), apparently, because they cannot form boron trifluoride complexes upon ligand exchange with boron-trifluoride etherate.

The structures of bis-hydroperoxides and their derivatives were determined on the basis of ^1H and ^{13}C NMR spectra, in particular, from the presence of signals with δ_C 111—122 typical of an sp^3-hybridized carbon atom bearing two oxygen functions and the correspondence of these spectra to published data. The presence of hydroperoxide groups in products **9—13** and **15** also followed from the IR absorption band at 3210—3429 cm^{-1} typical of these groups. The structure of bis-hydroperoxide **9e** was proved unambiguously by X-ray diffraction (Fig. 1). The principal geometric parameters are listed in Table 3. A specific feature of the crystal structure of this compound is layered packing in which the molecules of **9e** are connected by intermolecular hydrogen bonds.

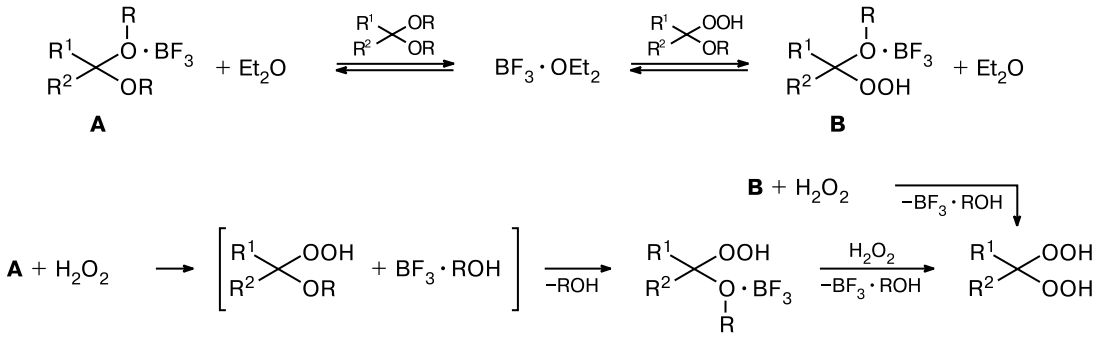
Bis-hydroperoxides **9a—h**, **11**, and **13a,b** are fairly stable at room temperature, their stabilities increase with the increase in the molecular mass. Thus **9e** and **9h** can be stored at room temperature without noticeable decomposition for 6 months, while **9c** and **11** are stable for 3—4 months when stored at −5—0 °C, while the half-life of **9a** is about a month even when kept in the cold. The stabilities of bis(1-hydroperoxycycloalkyl) peroxides **10**

Scheme 3



Reagents and conditions: Et_2O, H_2O_2 (2.5—3 equiv.), $BF_3 \cdot Et_2O$ (MeOH) (0.1—0.3 equiv.), ~20 °C, 1—3 h.

Scheme 4



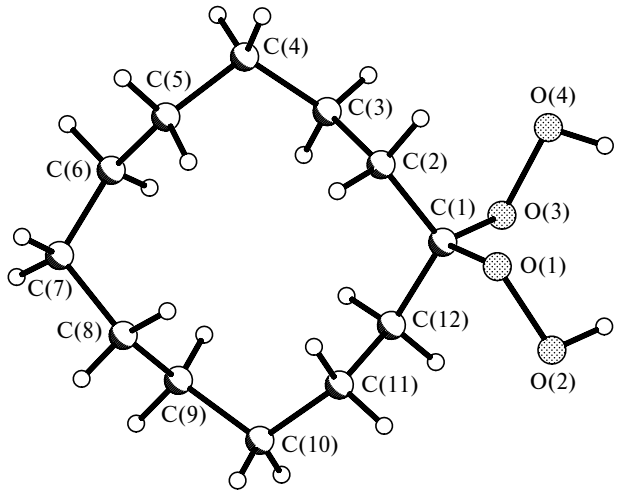


Fig. 1. Molecular structure of compound **9e**.

and **12**, bis(1-hydroperoxyalkyl) peroxides **15a,b**, and tetraalkyl-1,2,4,5-tetroxanes **16a,b** vary in a similar way. The presence of acid admixtures sharply decreases the stabilities of both bis-hydroperoxides and their derivatives. It is significant that bis-hydroperoxides **9**, **11**, and **13** and their derivatives **10**, **12**, and **14—16** are shock- and scratch-sensitive and require careful handling. Dispirotetroxane **14g** and tetraalkyltetroxanes **16a,b** decompose with explosion on heating to ≥100 °C.

Thus, this study dealing with the reactions of acetals and enol ethers with H_2O_2 catalyzed by boron trifluoride complexes resulted in the development of two new methods for the synthesis of aliphatic and alicyclic bis-hydroperoxides and their derivatives, namely, bis(1-hydroperoxycycloalkyl) and bis(1-hydroperoxyalkyl) peroxides and dispiro- and tetraalkyl-1,2,4,5-tetroxanes. The most important advantages of the new methods over the known

Table 3. Selected bond lengths (*d*) and bond angles (ω) in peroxide **9e**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
O(1)—C(1)	1.4368(16)	C(4)—H(4A)	1.02(2)	O(1)—C(1)—C(2)	102.32
O(1)—O(2)	1.4572(14)	C(4)—H(4B)	1.01(2)	O(1)—C(1)—O(3)	110.05
O(3)—C(1)	1.4099(17)	C(5)—H(5A)	0.98(2)	O(1)—C(1)—C(12)	112.50
O(3)—O(4)	1.4655(15)	C(5)—H(5B)	1.00(2)	O(3)—C(1)—C(2)	114.42
C(1)—C(2)	1.5187(19)	C(6)—H(6A)	0.93(2)	O(3)—C(1)—C(12)	102.48
C(1)—C(12)	1.5209(18)	C(6)—H(6B)	1.01(2)	C(1)—O(1)—O(2)	110.08
C(2)—C(3)	1.533(2)	C(7)—H(7A)	1.00(2)	C(1)—O(3)—O(4)	109.09
C(3)—C(4)	1.532(2)	C(7)—H(7B)	0.99(2)	C(1)—C(2)—C(3)	114.19
C(4)—C(5)	1.522(3)	C(8)—H(8A)	0.94(2)	C(1)—C(12)—C(11)	114.63
C(5)—C(6)	1.526(2)	C(8)—H(8B)	0.98(2)	C(2)—C(3)—C(4)	112.33
C(6)—C(7)	1.522(3)	C(9)—H(9A)	0.98(2)	C(3)—C(4)—C(5)	114.59
C(7)—C(8)	1.529(3)	C(9)—H(9B)	1.06(2)	C(4)—C(5)—C(6)	114.70
C(8)—C(9)	1.528(2)	C(10)—H(10A)	1.00(2)	C(5)—C(6)—C(7)	114.34
C(9)—C(10)	1.527(2)	C(10)—H(10B)	0.91(2)	C(6)—C(7)—C(8)	114.04
C(10)—C(11)	1.531(2)	C(11)—H(11A)	0.93(2)	C(7)—C(8)—C(9)	114.47
C(11)—C(12)	1.527(2)	C(11)—H(11B)	0.98(2)	C(8)—C(9)—C(10)	113.68
C(2)—H(2A)	1.00(2)	C(12)—H(12A)	0.964(17)	C(10)—C(11)—C(12)	112.14
C(2)—H(2B)	0.966(17)	C(12)—H(12B)	1.035(19)	O(1)—O(2)—HO(2)	103.10
C(3)—H(3A)	1.02(2)	O(2)—H(2O)	0.87(2)		
C(3)—H(3B)	0.92(2)	O(4)—H(4O)	0.83(2)		

methods[7—12] include simplicity of the reaction procedures, short time required (1—2 h), and higher (or comparable) product yields (70—95%).

Experimental

NMR spectra were recorded on Bruker WM-250 (250.13 MHz for ^{1}H) and Bruker AM-300 (75.4 MHz for ^{13}C) spectrometers for solutions in $CDCl_3$. IR spectra were measured on a UR-20 spectrometer (Carl Zeiss, Jena) in thin films. TLC analysis was performed on Silufol UV-254 plates. For flash chromatography, silica gel L 40/100 μm was used.

Cycloalkanones **1a—e,g**, 4-methylpentan-2-one, pentadecan-7-one (Aldrich), acetals **6a** and **7a,b**, $BF_3 \cdot OEt_2$, and $BF_3 \cdot MeOH$ (Acros) were commercial chemicals. Ketones **1f**,[13] **1h**,[14] and **1i** [15] were prepared by reported procedures.

The starting acetals and enol ethers were synthesized by known methods from the corresponding ketones,[16—18] and solutions of H_2O_2 in Et_2O were prepared by a known procedure.[19] The physical and spectral properties of known compounds corresponded to published data;[20] those for new compounds are presented below.

1,1-Dimethoxy-2-octylcyclopentane (2f). Oil, b.p. 151—153 °C (10 Torr). ^{1}H NMR, δ: 0.88 (t, 3 H, Me, J = 7.2 Hz); 1.16—1.93 (m, 21 H, CH_2, CH); 3.18, 3.22 (both s, 3 H each, OMe).

1,1-Dimethoxy-2-nonylcyclododecane (2h). Oil, b.p. 115—118 °C (0.01 Torr). ^{1}H NMR, δ: 0.87 (t, 3 H, Me, J = 7.2 Hz); 1.16—1.93 (m, 39 H, CH_2, CH); 3.18, 3.19 (both s, 3 H each, OMe).

2-Methyl-1-methoxycyclohexene (4g). Oil, b.p. 61—64 °C (10 Torr). ^{1}H NMR, δ: 1.42—2.30 (m, 11 H, CH_2, Me); 3.52 (s, 3 H, OMe).

8,8-Dimethoxypentadecane (7b). Oil, b.p. 114—116 °C (10 Torr). ^{1}H NMR, δ: 0.87 (t, 3 H, Me, J = 7.2 Hz); 1.15—2.10 (m, 24 H, CH_2, Me); 3.12 (s, 6 H, OMe).

8-Methoxypentadec-7-ene (8b). Oil, b.p. 161—165 °C (10 Torr). ^{1}H NMR, δ: 0.87—2.15 (m, 22 H, CH_2, Me); 3.82 (s, 3 H, OMe); 4.41—4.46 (m, 1 H, CH).

Synthesis of bis-hydroperoxides and their derivatives (general procedure, see Tables 1 and 2). *A*. A solution of a acetal or enol ether (10 mmol) in 40 mL of Et_2O was added dropwise at ~20 °C over a period of ~5 min to a stirred solution containing H_2O_2 (1.5—8 equiv.) and $BF_3 \cdot OEt_2$ or $BF_3 \cdot MeOH$ (0.1—0.3 equiv.) in Et_2O (50 mL). The reaction mixture was stirred up to complete conversion of the acetal or enol ether (1—2 h for acetals and 0.5—1 h for enol ethers, TLC), then K_2CO_3 (2 equiv.) and water (40—50 mL) were added, the resulting two-phase system was stirred for 0.5—1 h, and the organic phase was separated. The aqueous phase was extracted with Et_2O (3×10 mL), the extracts were combined with the organic phase, and the combined solution was dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography of the residue (gradient elution with a light petroleum—Et_2O mixture with the ether content increasing from 30 to 70%) gave target bis-hydroperoxides **9**, **11**, and **13** and their derivatives **10**, **12**, and **14—16**.

B. Potassium carbonate (2 equiv.) was added to the reaction mixture obtained according to procedure *A* after completion of the conversion of the acetal or enol ether, the resulting heterogeneous mixture was stirred for 0.5 h and filtered, and the filtrate was concentrated. Flash chromatography of the residue gave the target bis-hydroperoxides and their derivatives.

C. A solution of NaOH (3 equiv.) in 30—50 mL of water was added to the reaction mixture obtained according to procedure *A* after completion of the conversion of the acetal or enol ether, the aqueous phase was separated and washed with Et_2O (3×15 mL) to remove organic material from the bis-hydroper-

oxide Na salt. Then Et_2O (50—70 mL) was added, and a 2—5% aqueous solution of H_2SO_4 was added with cooling and stirring to pH 5—6. The ethereal layer was separated, washed with water (2×10 mL), a saturated aqueous solution of $NaHCO_3$ (2×10 mL), and again with water (10 mL), dried with anhydrous $MgSO_4$, and concentrated to give white crystals of bis-hydroperoxide **9e** and/or its derivative **12e** containing a small amount of water. Analytical samples were obtained by evacuation of these products for 3—4 h (0.1 Torr) at ~20 °C.

1,1-Dihydroperoxycyclopentane (9a).[12] Oil. Found (%): C, 44.90; H, 7.57. $C_5H_{10}O_4$. Calculated (%): C, 44.77; H, 7.51. IR (NaCl), ν/cm^{-1}: 3420 (OOH). ^{1}H NMR, δ: 1.68—1.80 (m, 4 H, CH_2); 1.93—2.11 (m, 4 H, C—CH_2); 9.89—9.94 (br.s, 2 H, OOH). ^{13}C NMR, δ: 24.6, 33.4 (CH_2), 122.6 (C).

1,1-Dihydroperoxycyclohexane (9b).[12] Oil. Found (%): C, 48.95; H, 8.20. $C_6H_{12}O_4$. Calculated (%): C, 48.64; H, 8.16. IR, NaCl), ν/cm^{-1}: 3424 (OOH). ^{1}H NMR, δ: 1.32—1.60 (m, 6 H, CH_2); 1.74—1.87 (m, 4 H, C—CH_2); 9.44—9.60 (br.s, 2 H, OOH). ^{13}C NMR, δ: 22.3, 25.1, 29.3 (CH_2), 111.0 (C).

1,1-Dihydroperoxycycloheptane (9c).[8] Oil. Found (%): C, 52.12; H, 8.84. $C_7H_{14}O_4$. Calculated (%): C, 51.84; H, 8.70. IR (NaCl), ν/cm^{-1}: 3429 (OOH). ^{1}H NMR, δ: 1.51—1.65 (m, 8 H, CH_2); 1.86—2.00 (m, 4 H, C—CH_2); 9.80—9.90 (br.s, 2 H, OOH). ^{13}C NMR, δ: 22.5, 29.9, 32.4 (CH_2), 115.8 (C).

1,1-Dihydroperoxycyclooctane (9d).[8] Oil. IR (NaCl), ν/cm^{-1}: 3400 (OOH). ^{1}H NMR, δ: 1.45—1.62 (m, 10 H, CH_2); 1.78—1.99 (m, 4 H, C—CH_2); 9.59—9.70 (br.s, 2 H, OOH). ^{13}C NMR, δ: 21.7, 24.8, 27.1, 27.8 (CH_2), 114.6 (C). Found (%): C, 54.74; H, 9.18. $C_8H_{16}O_4$. Calculated (%): C, 54.53; H, 9.15.

1,1-Dihydroperoxycyclododecane (9e).[8,10,12] White crystals, m.p. 138—142 °C (diethyl ether), 140—141 °C (benzene).[8] Found (%): C, 62.12; H, 10.40. $C_{12}H_{24}O_4$. Calculated (%): C, 62.04; H, 10.41. IR (NaCl), ν/cm^{-1}: 3410 (OOH). ^{1}H NMR, δ: 1.21—1.82 (m, 22 H, CH_2); 9.98—10.04 (br.s, 2 H, OOH). ^{13}C NMR, δ: 20.0, 22.2, 22.5, 26.4, 26.5, 27.4 (CH_2), 113.6 (C).

1,1-Dihydroperoxy-2-octylcyclopentane (9f). Oil. Found (%): C, 63.49; H, 10.66. $C_{13}H_{26}O_4$. Calculated (%): C, 63.38; H, 10.64. IR (NaCl), ν/cm^{-1}: 3428 (OOH). ^{1}H NMR, δ: 0.86—0.91 (t, 3 H, Me); 1.15—1.33 (m, 21 H, CH, CH_2); 9.63—9.70 (br.s, 2 H, OOH). ^{13}C NMR, δ: 14.0 (Me), 21.9, 22.6, 28.1, 29.2, 29.3, 29.5, 29.7, 31.0, 31.8, 32.7 (CH_2), 46.4 (CH), 121.2 (C).

1,1-Dihydroperoxy-2-methylcyclohexane (9g). Oil. Found (%): C, 52.06; H, 8.82. $C_7H_{14}O_4$. Calculated (%): C, 51.84; H, 8.70. IR (NaCl), ν/cm^{-1}: 3418 (OOH). ^{1}H NMR, δ: 0.89—0.94 (d, 3 H, Me); 1.33—1.71 (m, 9 H, CH, CH_2); 8.72—8.83 (br.s, 2 H, OOH). ^{13}C NMR, δ: 22.0 (Me), 29.4, 30.5, 31.5, 34.0 (CH_2), 37.4 (CH), 111.5 (C).

1,1-Dihydroperoxy-2-nonylcyclododecane (9h). Oil. Found (%): C, 69.97; H, 11.58; $C_{21}H_{42}O_4$. Calculated (%): C, 70.34; H, 11.81. IR (NaCl), ν/cm^{-1}: 3415 (OOH). ^{1}H NMR, δ: 0.18—1.82 (m, 40 H, CH, CH_2, Me); 8.75—9.20 (br.s, 2 H, 2 OOH). ^{13}C NMR, δ: 14.2 (Me), 19.4, 20.0, 21.8, 22.0, 22.1, 22.2, 22.3, 22.4, 22.5, 22.8, 25.4, 26.0, 26.2, 26.5, 27.4, 29.2, 29.4, 29.8, 32.0 (CH, CH_2), 115.2 (C).

Bis(2-hydroperoxyadamantan-2-yl) peroxide (10). Oil. Found (%): C, 65.71; H, 8.17; $C_{20}H_{30}O_6$. Calculated (%): C, 65.55; H, 8.25. IR (NaCl), ν/cm^{-1}: 3420 (OOH). ^{1}H NMR, δ: 1.62—2.16 (m, 28 H, CH_2); 9.02—9.15 (br.s, 2 H, OOH). ^{13}C NMR, δ: 27.2, 31.3 (CH), 33.8, 37.2 (CH_2), 112.0 (C).

2,2-Dihydroperoxyadamantane (11).[8] Oil. Found (%): C, 59.66; H, 7.98. $C_{10}H_{16}O_4$. Calculated (%): C, 59.98; H, 8.05. IR (NaCl), ν/cm^{-1}: 3420 (OOH). ^{1}H NMR, δ: 1.62—2.06 (m, 14 H, CH_2); 9.02—9.11 (br.s, 2 H, OOH). ^{13}C NMR, δ: 26.9, 31.1 (CH), 33.6, 36.9 (CH_2), 112.9 (C).

Bis(1-hydroperoxycyclopentyl) peroxide (12a).[12] Oil. Found (%): C, 51.41; H, 7.79. $C_{10}H_{18}O_6$. Calculated (%): C, 51.27; H, 7.75. IR (NaCl), ν/cm^{-1}: 3428 (OOH). ^{1}H NMR, δ: 1.71—1.82 (m, 4 H, C—CH_2); 1.93—2.12 (m, 4 H, CH_2); 9.85—10.02 (br.s, 2 H, OOH). ^{13}C NMR, δ: 24.5, 33.3 (CH_2), 122.2 (C).

Bis(1-hydroperoxycyclohexyl) peroxide (12b)[12,21,22]**.** Oil. Found (%): C, 55.13; H, 8.49. $C_{12}H_{22}O_6$. Calculated (%): C, 54.95; H, 8.45. IR, NaCl), ν/cm^{-1}: 3422 (OOH). ^{1}H NMR (δ: 1.43—1.67 (m, 6 H, CH_2); 1.79—1.93 (m, 4 H, C—CH_2); 9.40—9.62 (br.s, 2 H, OOH). ^{13}C NMR (δ: 22.5, 25.4, 29.9 (CH_2), 111.2 (C).

Bis(1-hydroperoxycyclooctyl) peroxide (12d). Oil. Found (%): C, 59.66; H, 7.98. $C_{16}H_{30}O_6$. Calculated (%): C, 60.35; H, 9.50. IR (NaCl), ν/cm^{-1}: 3448 (OOH). ^{1}H NMR, δ: 1.52—1.69 (m, 8 H, C—CH_2); 1.80—2.06 (m, 20 H, CH_2); 9.48—9.60 (br.s, 2 H, OOH). ^{13}C NMR, δ: 21.9, 24.9, 27.7, 27.9 (CH_2), 115.5 (C).

Di(1-hydroperoxy-2-methylcyclohexyl) peroxide (12g). Oil. Found (%): C, 65.22; H, 9.31; $C_{14}H_{26}O_6$. Calculated (%): C, 65.60; H, 9.44. IR (NaCl), ν/cm^{-1}: 3415 (OOH). ^{1}H NMR, δ: 0.83—2.31 (m, 24 H, CH, CH_2, Me); 9.47—9.60 (br.s, 2 H, OOH). ^{13}C NMR, δ: 22.0 (Me), 29.2, 30.5, 31.6, 34.0, 37.6 (CH, CH_2), 111.6 (C).

2,2-Dihydroperoxy-4-methylpentane (13a). Oil. Found (%): C, 47.70; H, 9.51. $C_6H_{14}O_4$. Calculated (%): C, 47.99; H, 9.40. IR (NaCl), ν/cm^{-1}: 3340 (OOH). ^{1}H NMR, δ: 0.92—0.99 (d, 6 H, Me); 1.46 (s, 3 H, C—Me); 1.66—1.70 (d, 2 H, CH_2); 1.76—1.80 (m, 1 H, CH); 9.19—9.31 (br.s, 2 H, OOH). ^{13}C NMR, δ: 18.0 (CH), 23.7 (2 Me), (Me), 41.1 (CH_2), 112.7 (C).

8,8-Dihydroperoxypentadecane (13b). Oil. Found (%): C, 65.32; H, 11.72. $C_{15}H_{32}O_4$. Calculated (%): C, 65.18; H, 11.67. IR (NaCl), ν/cm^{-1}: 3405 (OOH). ^{1}H NMR, δ: 0.83—0.83 (t, 6 H, Me); 1.23—1.40 (m, 20 H, CH_2); 1.52—1.67 (m, 4 H, C—CH_2); 9.60—9.80 (br.s, 2 H, OOH). ^{13}C NMR, δ: 14.0 (Me), 22.6, 23.8, 29.0, 29.2, 29.6, 31.6 (CH_2), 113.4 (C).

1,10-Dimethyl-7,8,15,16-tetraoxadispiro[5.2.5.2]hexadecane (14g). Oil. Found (%): C, 65.91; H, 9.50. $C_{14}H_{24}O_4$. Calculated (%): C, 65.60; H, 9.44. ^{1}H NMR, δ: 0.85—0.93 (d, 6 H, Me); 1.20—1.75 (m, 18 H, CH, CH_2) ^{13}C NMR, δ: 19.9 (Me), 28.9, 30.5, 31.9, 34.0 (CH_2), 37.7 (CH), 113.2 (C).

Bis(2-hydroperoxy-4-methylpentan-2-yl) peroxide (15a). Oil. Found (%): C, 53.95; H, 9.71. $C_{12}H_{26}O_6$. Calculated (%): C, 54.12; H, 9.84. IR (NaCl), ν/cm^{-1}: 3416 (OOH). ^{1}H NMR, δ: 0.96 (d, 12 H, Me, J = 6.6 Hz); 1.45 (s, 6 H, CMe); 1.69 (d, 4 H, CH_2, J = 5.8 Hz); 1.75—1.89 (m, 2 H, CH); 8.10—8.41 (br.s, 2 H, OOH). ^{13}C NMR, δ: 17.8, 23.6, 24.1, 41.2 (CH, CH_2, Me), 112.2 (C).

Bis(8-hydroperoxypentadecan-8-yl) peroxide (15b). Oil. Found (%): C, 69.68; H, 12.13. $C_{30}H_{62}O_6$. Calculated (%): C, 69.45; H, 12.05. IR (NaCl), ν/cm^{-1}: 3416 (OOH). ^{1}H NMR, δ: 0.83—0.97 (t, 12 H, Me); 1.21—1.44 (m, 54 H, CH_2); 1.63—1.75 (m, 8 H, C—CH_2); 9.59—9.64 (br.s, 2 H, OOH). ^{13}C NMR, δ: 14.1 (Me), 22.6, 23.5, 29.0, 29.3, 29.6, 31.7 (CH_2), 114.6 (C).

3,6-Diisobutyl-3,6-dimethyl-1,2,4,5-tetroxane (16a). Oil. Found (%): C, 62.31; H, 10.52. $C_{12}H_{24}O_4$. Calculated (%): C, 62.04; H, 10.41. IR (NaCl), ν/cm^{-1}: 3342 (OOH). ^{1}H NMR, δ: 0.96 (d, 12 H, Me, J = 6.6 Hz); 1.43 (s, 6 H, Me); 1.67 (d, 4 H, CH_2, J = 5.9 Hz); 1.74—1.87 (m, 2 H, CH). ^{13}C NMR, δ: 17.9, 23.7, 24.1, 41.3 (CH, CH_2, Me), 112.7 (C).

3,3,6,6-Tetraheptyl-1,2,4,5-tetroxane (16b). ^{1}H NMR, δ: 0.84—0.93 (t, 12 H, Me); 1.22—1.43 (m, 54 H, CH_2); 1.52—1.71 (m, 8 H, C—CH_2). ^{13}C NMR, δ: 14.0 (Me), 22.6, 23.5, 29.0, 29.5, 29.6, 31.7 (CH_2), 114.7 (C).

Transformations of bis-hydroperoxide 13a on treatment with $BF_3 \cdot OEt_2$. A solution of **13a** (1 mmol) and $BF_3 \cdot OEt_2$ (0.2 mmol) in ether (10 mL) was stirred for 15 min at ~20 °C. After the workup and analysis of the reaction mixture carried out by procedure *A*, unchanged bis-hydroperoxide (0.4 mmol) and approximately equal amounts of peroxide **15a** and tetroxane **16a** were identified. Under analogous conditions in the absence of $BF_3 \cdot OEt_2$, the transformation of **13a** into **15a** and **16a** did not take place.

X-Ray diffraction analysis of 1,1-dihydroperoxycyclododecane (9e). The crystals of compound **9e** ($C_{12}H_{24}O_4$) are orthorhombic. At 170 K, a = 5.9243(14), b = 13.211(3), c = 16.271(3) Å, V = 1273.5(5) Å^3, d_{calc} = 1.212 g cm^{-3}, μ = 0.089 mm^{-1}, space group $P2_12_12_1$, Z = 4.

The intensities of the 2160 independent reflections were measured on a Syntex $P2_1$ four-circle diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, θ/2θ scan mode, $2\theta_{max}$ 60°, completeness of the collected reflections 100%) equipped with a low-temperature nitrogen attachment. The reflection intensities were corrected using Lorentzian and polarization factors. No absorption corrections were applied.

The structure of molecule **9e** (see Fig. 1) was solved by the direct method. The nonhydrogen atoms were refined by the full-matrix least-squares method over F^2 in the anisotropic approximation. The hydrogen atoms were located from the difference Fourier synthesis and refined isotropically. The final R-factors were R_1 = 0.035 (calculated over F for 1875 reflections with $I > 2\sigma(I)$), wR_2 = 0.087 (calculated over F^2 for all the 2160 reflections involved in the final refinement stage), the number of refined parameters was 241, GOOF 0.968. All calculations were carried out using the SHELXTL-97 program package.[23] The crystal data and structure refinement parameters of compound **9e** are deposited with the Cambridge Structural Database.

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