New Preparation of 1,2,4,5-Tetraoxanes

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Abstract: A convenient procedure was developed for the synthesis of 1,2,4,5-tetraoxanes based on the reaction of *gem*-bishydroperoxycycloalkanes with ketals and acetals catalyzed by boron trifluoride etherate, which makes it possible to prepare the target products in yields from 13 to 93%.

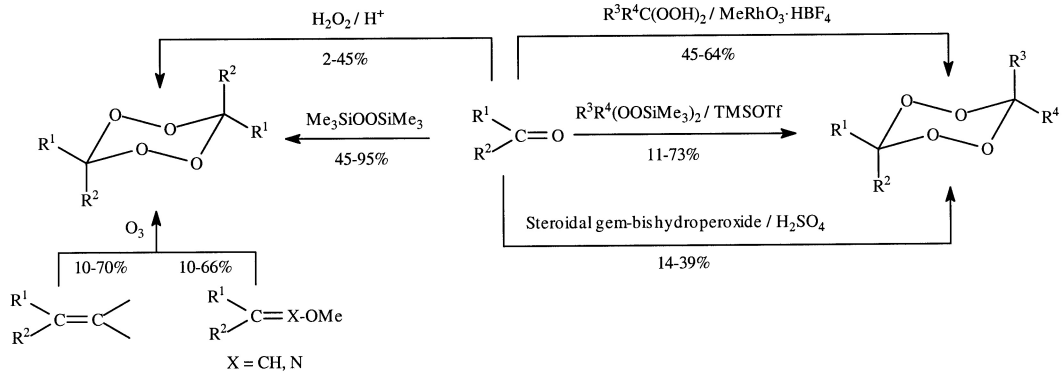
Key words: tetraoxanes, heterocycles, peroxides, acetals, boron

In the last 15 years, cyclic peroxides have attracted considerable attention of chemists and pharmacologists because of their high antimalarial, antiproliferative, and antimycobacterial activities, and the synthesis and pharmacological activities of this type of compounds, in particular, of 1,2,4,5-tetraoxanes, have been subjects of extensive research.[1–17]

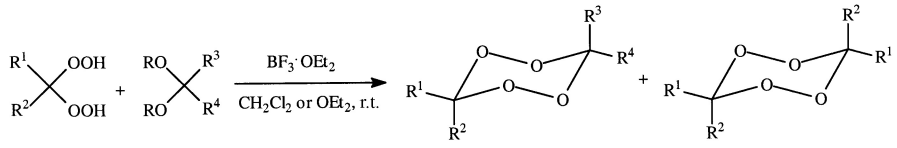
To date, more than 150 symmetrical and unsymmetrical 1,2,4,5-tetraoxanes have been synthesized. Most symmetrical tetraoxanes were prepared by acid-catalyzed cyclocondensation of hydrogen peroxide with ketones and benzaldehydes;[3,7,13–15,18–25] cyclocondensation of bis(trimethylsilyl) peroxide with carbonyl compounds promoted by trimethylsilyl trifluoromethanesulfonate (TMSOTf);[2,6b,11] ozonolysis of olefins,[22,26] enol ethers,[27,28] and O-ether oximes[5,12,29] (Scheme 1). A number of other methods were also used for the synthesis of these compounds.[27,30–32] Only three preparative routes to unsymmetrical tetraoxanes are known. These routes are based on catalytic cyclocondensation of ketones and aldehyde with steroidal *gem*-bishydroperoxides (H_2SO_4 as the catalyst),[11] aliphatic and alicyclic *gem*-dihydroperoxides (the $MeRhO_3$–HBF_4 system as the catalyst),[33] and *gem*-bis(trimethylsilyldioxy)alkanes (TMSOTf as the catalyst) prepared by treatment of bishydroperoxides with *N*,*O*-bis(trimethylsilyl)acetamide (BSA).[6a]

We developed a new convenient and simpler approach to tetraoxanes, which allows one to prepare these compounds (in most cases, in higher yields) with the use of more readily accessible and inexpensive starting compounds (Scheme 2). This approach is based on the reactions of *gem*-bishydroperoxides with aldehyde or ketone acetals catalyzed by boron trifluoride etherate.

We studied the cyclocondensation of cycloalkylidene bishydroperoxides **1** with cycloalkanone dimethyl and diethyl acetals **2**, aliphatic and alkylaromatic aldehydes and ketones **3**, and adamantanone dimethyl acetal **4**. The main results of this investigation are given in Table 1.



Scheme 1



Scheme 2

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Table 1 $BF_3{\cdot}OEt_2$ Catalyzed Cyclocondensation of Cycloalkylidene Bishydroperoxides **1**– and Acetals **2–4**[a]

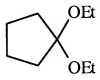
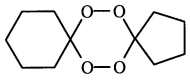
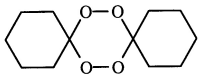
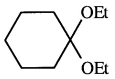
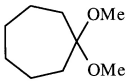
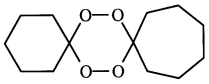
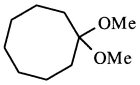
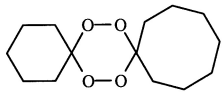
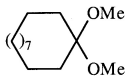
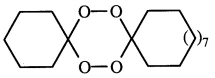
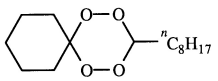
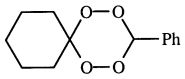
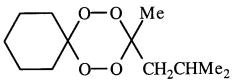
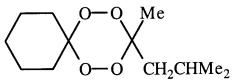
Entry	Acetal	Solvent	$BF_3{\cdot}OEt_2$ (equiv)	t (min)	Procedure[b]	Tetraoxanes,[c] yield (%)	Ratio[d]
Cyclohexylidene-1,1-bishydroperoxide (**1a**)							
1	 **2a**	Et_2O	0.3	40	A	 **5a**, 52  **5b**, 12	4.3
2	 **2b**	Et_2O	0.4	40	A	**5b**, 68	–
3	 **2c**	Et_2O	0.3	45	B	 **5c**, 50 **5b**, 20	2.5
4	 **2d**	Et_2O	0.3	50	B	 **5d**, 50 **5b**, 16	3.1
5	 **2e**	Et_2O	0.3	60	A	 **5e**, 90	–
6	**2e**	CH_2Cl_2	0.3	10	C	**5e**, 80 **5b**, 3	–
7	n-$C_8H_{17}CH(OMe)_2$ **3a**	Et_2O	0.4	60	A	 **6a**, 52 **5b**, 18	2.8
8	$PhCH(OMe)_2$ **3b**	Et_2O	1.4	50	A	 **6b,** 22 **5b,** 20	1.1
9	 **3c**	Et_2O	0.3	45	C	 **6c**, 49 **5b**, 24	2.0
10	**3c**	Et_2O	0.3	20	C	**6c**, 35 **5b**, 28	1.25
11	**3c**	CH_2Cl_2	0.3	10	D	**6c**, 63 **5b**, 9	7.0
12	**3c**	CH_2Cl_2	0.3	60	D	**6c**, 20 **5b**, 34	0.6

Table 1 $BF_3{\cdot}OEt_2$ Catalyzed Cyclocondensation of Cycloalkylidene Bishydroperoxides **1**– and Acetals **2**–**4**[a] (continued)

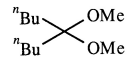
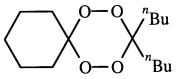
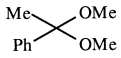
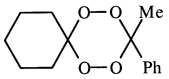
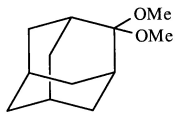
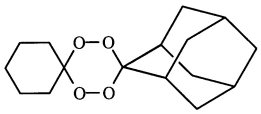
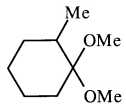
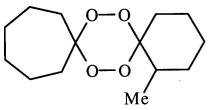
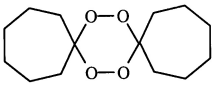
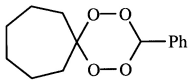
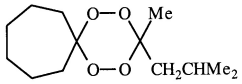
Entry	Acetal	Solvent	$BF_3{\cdot}OEt_2$ (equiv)	t (min)	Procedure[b]	Tetraoxanes,[c] yield (%)	Ratio[d]
13	 **3d**	Et_2O	0.3	50	A	 **6d**, 67 **5b,** 9	7.4
14	**3d**	CH_2Cl_2	0.3	10	C	**6d**, 77 **5b**, 6	12.8
15	**3d**	Et_2O	0.3	60	C	**6d**, 77 **5b**, 10	5.9
16	**3d**	Et_2O	0.3	60	D	**6d**, 74 **5b**, 9	5.7
17	**3d**	Et_2O	0.3	60	A	**6d**, 66 **5b**, 14	4.7
18	**3d**	Et_2O	0.3	60	B	**6d**, 64 **5b**, 13	4.9
19	 **3e**	Et_2O	1.4	60	A	 **6e**, 35 **5b**, 16	2.2
20	 **4**	CH_2Cl_2	0.3	20	C	 **7a**, 29 **5b**, 30	1
Cycloheptylidene-1,1-bishydroperoxide (**1b**)							
21	 **2f**	Et_2O	0.3	50	A	 **8a, 49**  **9, 12**	4.1
22	$PhCH(OMe)_2$ **3b**	Et_2O	1.3	50	A	 **8b**, 30 **9**, 10	3
23	$Me_2CHCH_2C(OMe)_2Me$ **3c**	Et_2O	0.3	50	B	 **8c**, 61 **9**, 10	6.1
24	**3c**	CH_2Cl_2	0.03	20	C	**8c**, 51 **9**, 8	6.4
25	**3c**	Et_2O	0.03	60	C	**8c**, 48 **9**, 9	5.3

Table 1 $BF_3{\cdot}OEt_2$ Catalyzed Cyclocondensation of Cycloalkylidene Bishydroperoxides **1**– and Acetals **2**–**4**[a] (continued)

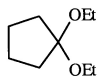
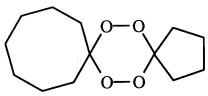
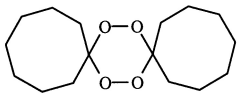
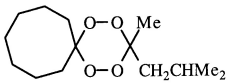
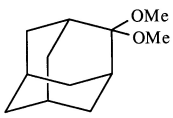
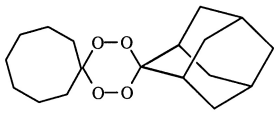
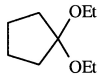
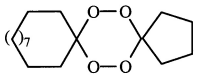
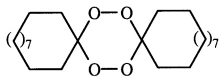
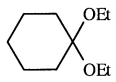
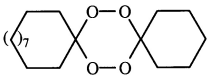
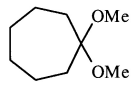
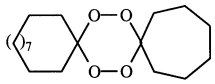
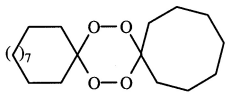
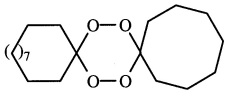
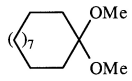
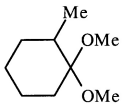
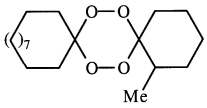
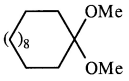
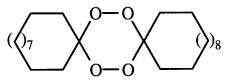
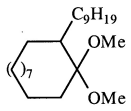
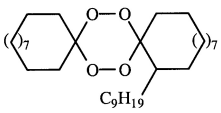
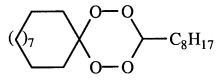
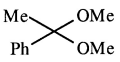
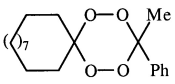
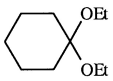
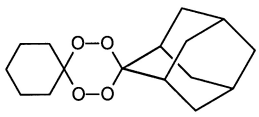
Entry	Acetal	Solvent	$BF_3{\cdot}OEt_2$ (equiv)	t (min)	Procedure[b]	Tetraoxanes,[c] yield (%)	Ratio[d]
26	**3c** (80 mmol)	CH_2Cl_2	0.2	20	D	**8c**, 80 **9**, 10	8
27	**3c** (10 mmol)	CH_2Cl_2	0.2	20	D	**8c**, 55 **9**, 10	5.5
Cyclooctalidene-1,1-bishydroperoxide (**1c**)							
28	 **2a**	Et_2O	0.3	60	B	 **10a**, 46  **11**, 8	5.9
29	$Me_2CHCH_2C(OMe)_2Me$ **3c**	Et_2O	0.3	60	A	 **10b**, 40 **11**, 7	5.7
30	 **4**	Et_2O	0.3	60	C	 **7b**, 32 **11**, 10	3.2
Cyclododecylidene-1,1-bishydroperoxide (**1d**)							
31	 **2a**	Et_2O	0.3	55	A	 **12a**, 39  **12e**, 3	13
32	 **2b**	Et_2O	0.1	60	A	 **5e**, 78	–
33	**2b**	Et_2O	0.3	60	B	**5e**, 92	–
34	**2b**	Et_2O	0.5	60	A	**5e**, 93	–
35	**2b**	CH_2Cl_2	0.3	10	D	**5e**, 89 **12e**, 4	22
36	**2b**	Et_2O	0.3	60	D	**5e**, 77 **12e**, 8	9.6
37	**2b** (0.9 mmol)	Et_2O	0.3	60	A	**5e**, 80	–
38	**2b** (15 mmol)	Et_2O	0.3	60	A	**5e**, 93	–

Table 1 $BF_3{\cdot}OEt_2$ Catalyzed Cyclocondensation of Cycloalkylidene Bishydroperoxides **1**– and Acetals **2–4**[a] (continued)

Entry	Acetal	Solvent	$BF_3{\cdot}OEt_2$ (equiv)	t (min)	Procedure[b]	Tetraoxanes,[c] yield (%)	Ratio[d]
39	 **2c**	Et_2O	0.3	60	C	 **12c**, 90	–
40	 **2d**	Et_2O	0.3	60	C	 **12d**, 70	–
41	 **2e**	Et_2O	0.3	60	A	**12e**, 46	–
42	 **2f**	Et_2O	0.3	60	D	 **12f**, 46 **12e**, 2	23
43	 **2g**	Et_2O	0.4	60	A	 **12g**, 35 **12e**, 2	17.5
44	 **2h**	Et_2O	0.4	60	A	 **12h**, 13 **12e**, 6	2.3
45	*n*-C8H$_{17}$CH(OMe)$_2$ **3a**	Et_2O	0.3	60	A	 **13a**, 44 **12e**, 4	11
46	 **3e**	Et_2O	1.3	60	A	 **13b**, 41 **12e**, 19	1
Adamantylidene-1,1-bishydroperoxide (**1e**)							
47	 **2b**	Et_2O	0.3	20	C	 **7a**, 61	–

[a] In all experiments, temperature 20–25 °C, excluding entry 12 (0 °C).
[b] The procedures A, B, C and D are described in the experimental part.
[c] All yields were calculated on bishydroperoxides.
[d] Ratio of unsymmetrical tetraoxanes to symmetrical ones.

Cyclocondensation was performed in diethyl ether or dichloromethane at 20–25 °C by adding either a solution of acetal to a solution of bishydroperoxide and $BF_3{\cdot}OEt_2$ (methods A and B) or a solution of bishydroperoxide to a solution of acetal and $BF_3{\cdot}OEt_2$ (methods C and D) for 2–3 min (at 0 °C, for ca. 20 min) and using of a 1.1-fold excess of acetal and 0.03–1.4 equiv of the catalyst. Under these conditions, bishydroperoxides underwent complete conversion (TLC control) within 10–60 min after completion of the addition. Cross-cyclocondensation of bishy-

droperoxides with acetals afforded unsymmetrical 1,2,4,5-tetraoxanes. In all experiments with six-, seven-, and eight-membered cycloalkylidene bishydroperoxides **1a–c** and in some experiments with dodecylidene bishydroperoxide (**1d**), this reaction was accompanied by competitive homocyclocondensation of bishydroperoxides giving rise to symmetrical tetraoxanes. The total yield of tetraoxanes varied from 19% in the reaction of **1d** with 2-nonylcyclododecanone acetal (entry 44) to 90–93% in the reactions of bishydroperoxides **1b** and **1d** with acetals **3c** and **2b** (entries 26 and 35, respectively). The ratio between unsymmetrical and symmetrical tetraoxanes varied from 1:1 in the reaction of **1a** with adamantanone acetal (entry 20) to 23:1 in the reaction of **1d** with 2-methylcyclohexanone acetal (entry 42). The exceptions were the reaction of bishydroperoxide **1a** with cyclododecanone acetal (entry 5) and the reactions of bishydroperoxide **1d** with acetals **2b–e**. In these cases, only cross-cyclocondensation of bishydroperoxide and acetal occurred (entries 32–34 and 37–41). The use of a higher (eight-fold) excess of acetal with respect to bishydroperoxide in the reaction of cycloheptylidene bishydroperoxide with methyl isobutyl ketone acetal led to an increase in the ratio between unsymmetrical and symmetrical tetraoxanes **8c** and **9** from 5.5:1 to 8:1 (entries 27 and 26, respectively). The addition of bishydroperoxide to acetal for 20 min resulted in a decrease in the yield of tetraoxanes due to partial acetal tarring, as evidenced by the brown color of the reaction mixture (cf. entries 8 and 9). In dichloromethane, cross-cyclocondensation of bishydroperoxides and ketals proceeds more rapidly and more selectively than that in diethyl ether (cf. entries 14 and 15, 24 and 25, 35 and 36). In the absence of $BF_3{\cdot}OEt_2$, neither homocyclocondensation of bishydroperoxides nor their cross-cyclocondensation with acetals occurs. The optimum amount of the catalyst with respect to acetal is 0.3 equiv. Unsymmetrical tetraoxanes are much more difficult to prepare by the reactions of bishydroperoxides with benzaldehyde acetal (entries 8 and 22) or acetophenone acetal (entries 19 and 46), and these reactions require the use of 1.3–1.4 equiv of $BF_3{\cdot}OEt_2$. In the reactions with 0.3 equiv of the etherate, the formation of aryl-substituted tetraoxanes was not observed. The fact that homocyclocondensation and cross-cyclocondensation are catalyzed by $BF_3{\cdot}OEt_2$ provides evidence that the catalyst activates both bishydroperoxides and acetals likely as the results of the formation of boron trifluoride complexes with these substrates. Investigation aimed at confirming the involvement of boron trifluoride complexes with acetals and bishydroperoxides in the formation of 1,2,4,5-tetraoxanes, as well as a study of boron trifluoride complexes with 1,2,4,5-tetraoxanes are currently underway.

The structures of tetraoxanes **5–13** (among which **6a**,**d**,**e**, **8c**, **10b**, and **13b** were prepared as oils and all other compounds were prepared as white powders) were determined by ^1H and ^{13}C NMR spectroscopy. The molecular structures of **12c** and **12e** were established by X-ray diffraction analysis (Figure 1). Crystal data and structure refinement for **12c** and **12e** are listed in Table 2. Of the tetraoxanes synthesized, 23 have not been described earlier. Tetraoxanes **5–13** are rather stable, do not decompose at room temperature, and do not detonate in the course of purification and analysis. These compounds form stable complexes with boron trifluoride.

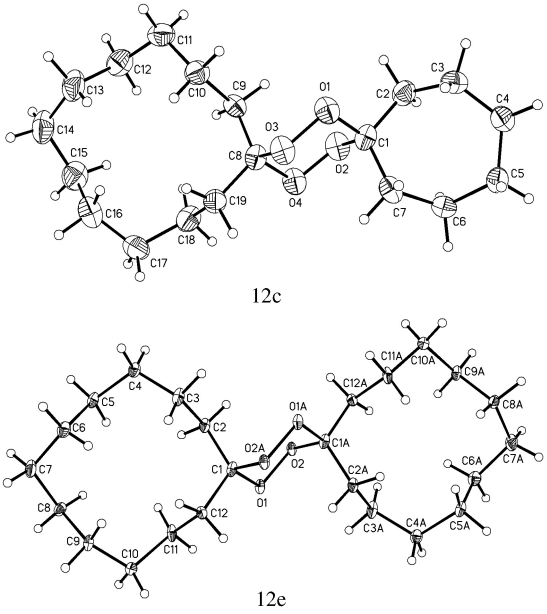


Figure 1 Molecular structures of tetraoxanes **12c** and **12**

Previously, only symmetrical tetraoxanes with six-, seven-, and eight-membered spiro rings (**5b**,[34a] **9**,[34b] and **11**,[34c] respectively) have been studied by X-ray diffraction analysis, whereas the three-dimensional structures of unsymmetrical tetraoxanes remained unknown. The conformation and geometric parameters of the symmetrical molecule with two 12-membered spiro rings (**12**) are similar to those observed in other symmetrical molecules, whereas the chair-like conformation of the heterocycle in the unsymmetrical molecule with seven- and twelve-membered spiro rings (**12c**) is distorted (the torsion angles about the O–O bonds differ by 4º).

To summarize, we have developed a new practical and convenient approach to symmetrical and unsymmetrical 1,2,4,5-tetraoxanes using cycloalkylidene bishydroperoxides as the starting reagents in their $BF_3{\cdot}OEt_2$-catalyzed cross-cyclocondensation with acetals. The reaction proceeds under mild conditions and makes a significant contribution to the available methods for the preparation of 1,2,4,5-tetraoxanes.

The NMR spectra were recorded on Bruker WM-250 (250.13 MHz for ^1H) and Bruker AM-300 (75.4 MHz for ^{13}C) spectrometers in $CDCl_3$. X-ray diffraction study of **12c** and **12** was carried out on automated diffractometers. The complete crystallographic data were deposited with the Cambridge Crystallographic Data Centre [registration numbers CCDC 239946 (**12c**), 239947 (**12e**)]. The TLC analysis was carried out using Silufol UV-254 chromatographic plates. Flash chromatography was performed with the use of silica

Table 2 Crystal Data and Structure Refinement for **12c** and **12e**

Compound	**12c**	**12e**
formula	$C_{19}H_{34}O_4$	$C_{24}H_{44}O_4$
mol. wt	326.46	396.59
crystal colour, habit	colorless prism	colorless plate
crystal size (mm)	0.50 × 0.45 × 0.30	0.40 × 0.25 × 0.15
crystal system	monoclinic	triclinic
space group	$P2_1/n$	P–1
cell constants		
a (Å)	5.964(3)	5.620(4)
b (Å)	16.728(6)	6.983(4)
c (Å)	14.928(6)	14.420(9)
α (deg)	90	85.43(1)
β (deg)	93.010(7)	88.71(1)
γ (deg)	90	84.42(1)
V (Å^3)	1886(2)	561.4(6)
Z	4	1
D_{calcd} (g cm^{-3})	1.150	1.173
Diffractometer	CAD4 Enraf-Nonius	Bruker SMART 1000 CCD
Temp (K)	295	120
Radiation	Mo*K*α (λ = 0.71073)	Mo*K*α (λ = 0.71073)
Scan mode	θ-5/3θ	
$2\theta_{max}$ (deg)	50	50
abs. coeff., μ(Mo*K*α) (cm^{-1})	0.78	0.77
Absorption correction	none	difabs
T_{max} and T_{min}	–	0.928 and 0.181
Structure solution	direct method	direct method
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
No. reflections collect	3721	2577
No. Independent reflections	3291 (R_{int} = 0.0221)	1503 (R_{int} = 0.0544)
No. observed reflections [$I > 2\sigma(I)$]	1093	1002
No. of parameters	208	127
*R*1, *wR*2	0.0577, 0.1378	0.0628, 0.1401
F(000)	720	220
GOOF	0.966	0.988
Largest diff. peak and hole (eÅ^{-3})	0.375 and –0.208	0.194 and –0.202

gel L 40/100 m. Melting points were determined on a Kofler hot plate.

$BF_3{\cdot}OEt_2$ was purchased from Acros. Bishydroperoxides were prepared according to a procedure described in the studies.[35,36] The starting acetals were synthesized by acetalization of the corresponding carbonyl compounds.

1,1-Dimethoxynonane (3a)
Bp 87–88 °C (20 Torr).

^{1}H NMR: δ = 0.86 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.20–1.38 (m, 12 H, CH_2), 1.53–1.62 (m, 2 H, CH_2), 3.29 (s, 6 H, OCH_3), 4.33 (t, *J* = 5.9 Hz, 1 H, CH).

5,5-Dimethoxynonane (3d)
Bp 68–69 °C (20 Torr).

^{1}H NMR: δ = 0.87 (t, *J* = 6.6 Hz, 6 H, CH_3,), 1.12–1.35 (m, 8 H, CH_2), 1.48–1.58 (m, 4 H, CH_2), 3.10 (s, 6 H, CH_3).

^{13}C NMR: δ = 13.9 (CH_3), 22.9, 25.7, 32.1 (CH_2), 47.5 (OCH_3), 103.3 (C).

Synthesis of Tetraoxanes 5–13; General Procedures
Procedure A
A solution of acetal (10 mmol) in CH_2Cl_2 or Et_2O (40 mL) was added to a stirred solution of bishydroperoxide (9 mmol) and $BF_3{\cdot}OEt_2$ (0.1–1.4 equiv with respect to peroxide) in CH_2Cl_2 or Et_2O (50 mL) at r.t. for ca. 2 min. The reaction mixture was stirred until the conversion of bishydroperoxide was completed (10–60 min, TLC control) and then aq K_2CO_3 (50 mL, 2 equiv) was added. The resulting two-phase system was stirred for 30–60 min and the organic phase was separated. The aq phase was extracted with CH_2Cl_2 or Et_2O (3 × 10 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and concentrated. Column chromatography of the residue [gradient elution with a mixture of petroleum ether (bp 40–70 °C) and Et_2O with increasing concentration of the latter from 15% to 60%] afforded tetraoxanes **5**–**13** and other reaction products. Analytical samples of tetraoxanes were prepared by evacuation (0.1 Torr) at ca. 20 °C for 3–4 h.

Procedure B
An aq Et_2NH solution (20%) was added to the reaction mixture obtained according to procedure A until it reached pH 8–8.5. Then the reaction mixture was stirred for 10–20 min. The aq and organic phases were separated. The aqueous layer was extracted with petroleum ether (bp 40–70 °C) (2 × 15 mL). The extracts were combined with the organic phase and worked up as described in procedure A.

Procedure C
A solution of bishydroperoxide (9 mmol) in CH_2Cl_2 or Et_2O (40 mL) was added at r.t. for 2 min (in entry 10, for 20 min) to a stirred solution of acetal (10 mmol) and $BF_3{\cdot}OEt_2$ (0.03–0.3 equiv) in CH_2Cl_2 or Et_2O (50 mL). The reaction mixture was stirred until the conversion of bishydroperoxide was completed (10–60 min, TLC control) and thereafter aq K_2CO_3 was added. Then the reaction mixture was worked up as described in procedure A.

Procedure D
An aq Et_2NH solution (20%) was added to the reaction mixture obtained according to the procedure C until it reached pH 8–8.5. Then the reaction mixture was worked up as described in the procedure B.

6,7,14,15-Tetraoxadispiro[4.2.5.2]pentadecane (5a)
Mp 95–97 °C ($CHCl_3$); R_f = 0.80 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.31–1.80 (m, 18 H, CH_2).

^{13}C NMR: δ = 22.6, 24.5, 25.5, 30.6, 33.4, 107.9, 118.8.

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.79; H, 8.50.

7,8,15,16-Tetraoxadispiro[5.2.5.2]hexadecane (5b)
Mp 129–130 °C ($CHCl_3$) (Lit.[24] 131–132 °C); R_f = 0.85 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.11–1.57 (m, 12 H, CH_2), 2.36 (m, 8 H, CH_2).

^{13}C NMR: δ = 22.8, 25.3, 30.5, 108.1.

7,8,16,17-Tetraoxadispiro[5.2.6.2]heptadecane (5c)
Mp 68–70 °C ($CHCl_3$); R_f = 0.78 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.09–2.00 (m, 22 H, CH_2).

^{13}C NMR: δ = 22.0, 22.5, 25.4, 30.0, 30.7, 32.9, 107.6, 112.8.

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.70; H, 9.10.

7,8,17,18-Tetraoxadispiro[5.2.7.2]octadecane (5d)
Mp 89–92 °C ($CHCl_3$); R_f = 0.78 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.11–1.89 (m, 24 H, CH_2).

^{13}C NMR: δ = 22.0, 24.5, 25.1, 25.3, 27.0, 29.7, 30.0, 104.2, 110.6.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.30; H, 9.50.

7,8,21,22-Tetraoxadispiro[5.2.11.2]docosane (5)
Mp 103–104 °C ($CHCl_3$); R_f = 0.75 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.21–1.90 (m, 32 H, CH_2).

^{13}C NMR: δ = 19.3, 21.8, 22.0, 22.7, 25.3, 25.5, 25.8, 26.0, 31.7, 106.1, 113.4.

Anal. Calcd for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32. Found: C, 68.98; H, 10.25.

3-Octyl-1,2,4,5-tetraoxaspiro[5.5]undecane (6a)
Oil; R_f = 0.77 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 0.85 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.08–1.88 (m, 24 H, CH_2), 4.74 (t, *J* = 5.9 Hz, 1 H, CH).

^{13}C NMR: δ = 11.4, 22.6, 22.7, 24.9, 25.5, 28.6, 29.3, 29.4, 29.5, 30.4, 33.5, 107.8, 109.5.

Anal. Calcd for $C_{15}H_{28}O_4$: C, 66.14; H, 10.36. Found: C, 66.00; H, 10.29.

3-Phenyl-1,2,4,5-tetraoxaspiro[5.5]undecane (6b)
Mp 103–104 °C ($CHCl_3$) (Lit.[6a] 103–104 °C); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.41–1.72 (m, 10 H), 6.67 (s, 1 H), 7.40–7.52 (m, 5 H).

^{13}C NMR: δ = 19.6, 20.0, 23.1, 27.9, 29.6, 105.6, 106.5, 125.3, 126.4, 128.8, 129.8.

3-Isobutyl-3-methyl-1,2,4,5-tetraoxaspiro[5.5]undecane (6c)
Mp 77–79 °C ($CHCl_3$); R_f = 0.8 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 0.96 (d, *J* = 6.6 Hz, 6 H, CH_3), 1.32–1.91 (m, 16 H, CH, CH_2, CH_3).

^{13}C NMR: δ = 18.1, 22.5, 22.7, 25.2, 25.5, 29.8, 31.6, 31.7, 106.1, 109.2.

Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.40; H, 9.51.

3,3-Dibutyl-1,2,4,5-tetraoxaspiro[5.5]undecane (6d)
Oil; R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 0.81–0.95 (t, *J* = 6.6 Hz, 6 H, CH_3), 1.26–1.90 (m, 22 H, CH_2).

^{13}C NMR: δ = 13.7, 22.3, 22.6, 23.5, 25.4, 26.0, 30.6, 107.4, 110.4.

Anal. Calcd for $C_{15}H_{28}O_4$: C, 66.14; H, 10.36. Found: C, 65.99; H, 10.40.

3-Methyl-3-phenyl-1,2,4,5-tetraoxaspiro[5.5]undecane (6e)
Oil; R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:3).

^{1}H NMR: δ = 1.26–1.98 (m, 13 H, CH_2, CH_3), 7.31–7.49 (m, 3 H, CH), 7.54–7.68 (m, 2 H, CH).

^{13}C NMR: δ = 22.2, 25.3, 25.5, 30.6, 108.0, 115.2, 127.9, 128.2, 129.4, 133.0.

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.93; H, 7.18.

3-(1,1′-Adamant-2-yl)-1,2,4,5-tetraoxaspiro[5.5]undecane (7a)
Mp 67–69 °C ($CHCl_3$); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.21–2.48 (m, 22 H, CH, CH_2).

^{13}C NMR: δ = 22.7, 25.0, 27.4, 29.7, 30.9, 36.2, 37.0, 37.3, 104.3, 107.9.

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.38; H, 8.50.

3-(1,1′-Adamant-2-yl)-1,2,4,5-tetraoxaspiro[5.7]tridecane (7b)
Mp 85–87 °C ($CHCl_3$); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:3).

^{1}H NMR: δ = 1.16–2.25 (m, 28 H, CH, CH_2).

^{13}C NMR: δ = 22.7, 25.0, 27.4, 27.9, 28.9, 29.4, 29.7, 30.9, 33.5, 37.3, 103.1, 104.0.

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.01; H, 9.22.

1-Methyl-7,8,16,17-tetraoxadispiro[5.2.6.2]heptadecane (8a)
Mp 40–42 °C ($CHCl_3$); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:2).

^{1}H NMR: δ = 0.75–2.00 (m, 24 H, CH, CH_2, CH_3).

^{13}C NMR: δ = 22.1, 22.4, 22.6, 22.7, 29.8, 30.0, 31.7, 32.5, 32.8, 107.3, 112.5.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.81; H, 9.40.

3-Phenyl-1,2,4,5-tetraoxaspiro[5.6]dodecane (8b)
Mp 30–33 °C ($CHCl_3$); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.33–1.89 (m, 12 H, CH_2), 6.56 (s, 1 H, CH), 6.80–6.93 (m, 3 H, CH), 7.28–7.40 (m, 2 H, CH).

^{13}C NMR: δ = 22.6, 29.5, 32.5, 107.3, 113.8, 128.1, 129.0, 129.2, 131.5.

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.98; H, 7.50.

3-Isobutyl-3-methyl-1,2,4,5-tetraoxaspiro[5.6]dodecane (8c)
Oil; R_f = 0.92 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 0.96 (d, *J* = 6.6 Hz, 6 H, CH_3), 1.32–1.91 (m, 18 H, CH, CH_2, CH_3).

^{13}C NMR: δ = 18.9, 22.6, 22.8, 24.1, 29.9, 30.1, 32.8, 32.9, 109.4, 112.7.

Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 63.82; H, 9.92.

8,9,17,18-Tetraoxadispiro[6.2.6.2]hexadecane (9)
Mp 100–101 °C ($CHCl_3$) (Lit.[15] 103 °C); R_f = 0.85 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.22–2.29 (m, 24 H, CH_2).

^{13}C NMR: δ = 22.8, 30.1, 32.8, 112.8.

6,7,16,17-Tetraoxadispiro[4.2.7.2]heptadecane (10a)
Mp 45–47 °C ($CHCl_3$); R_f = 0.8 (TLC; Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.20–1.85 (m, 22 H, CH_2).

^{13}C NMR: δ = 24.6, 25.1, 28.1, 29.7, 33.2, 33.5, 106.6, 119.2.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 64.44; H, 9.15. Found: C, 64.70; H, 9.20.

3-Isobutyl-3-methyl-1,2,4,5-tetraoxaspiro[5.7]tridecane (10b)
Oil; R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 0.96 (d, *J* = 6.6 Hz, 6 H, CH_3), 1.20–1.91 (m, 20 H, CH, CH_2, CH_3).

^{13}C NMR: δ = 18.9, 22.0, 24.0, 24.6, 25.0, 26.7, 28.0, 28.1, 29.7, 109.3, 111.7.

Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14. Found: C, 65.22; H, 10.17.

9,10,19,20-Tetraoxadispiro[7.2.7.2]eicosane (11)
Mp 100–102 °C (Lit.[15] 98 °C); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:2).

^{1}H NMR: δ = 1.45–1.61 (m, 8 H, C–CH_2), 1.79–1.83 (m, 20 H, CH_2).

^{13}C NMR: δ = 21.9, 25.8, 27.4, 28.0, 115.3.

Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.85; H, 10.00.

6,7,20,21-Tetraoxadispiro[4.2.11.2]henicosane (12a)
Mp 57–59 °C ($CHCl_3$); R_f = 0.82 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.08–1.73 (m, 30 H, CH_2).

^{13}C NMR: δ = 19.1, 22.2, 22.4, 24.6, 24.7, 25.1, 25.3, 33.2, 112.0, 118.9.

Anal. Calcd for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.32; H, 10.08.

8,9,22,23-Tetraoxadispiro[6.2.11.2]tricosane (12c)
Mp 68–72 °C ($CHCl_3$); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.19–1.75 (m, 34 H, CH_2).

^{13}C NMR: δ = 19.3, 21.9, 22.2, 22.5, 24.6, 25.9, 26.4, 29.1, 30.0, 111.5, 112.6.

Anal. Calcd for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50. Found: C, 69.72; H, 10.38.

9,10,23,24-Tetraoxadispiro[7.2.11.2]tetracosane (12d)
Mp 148–151 °C ($CHCl_3$); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.30–1.64 (m, 36 H, CH_2).

^{13}C NMR: δ = 18.1, 19.4, 21.7, 22.2, 22.6, 24.3, 24.7, 25.5, 27.4, 29.7, 105.1, 112.6.

Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.43; H, 10.58.

13,14,27,28-Tetraoxadispiro[11.2.11.2]octacosane (12)
Mp 200–201 °C ($CHCl_3$) (Lit.[15] 201 °C); R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.18–1.93 (m, 44 H, CH_2).

^{13}C NMR: δ = 22.0, 22.2, 23.0, 25.4, 26.0, 30.4, 108.1.

1-Methyl-7,8,21,22-tetraoxadispiro[5.2.11.2]docosane (12f)
Mp 105–106 °C ($CHCl_3$); R_f = 0.85 (TLC, Et_2O–petroleum ether, 1:2).

^{1}H NMR: δ = 0.75–1.82 (m, 34 H, CH, CH_2, CH_3).

^{13}C NMR: δ = 19.3, 21.8, 22.0, 22.6, 24.2, 24.6, 24.7, 26.1, 26.3, 29.2, 30.9, 31.9, 108.0, 111.5.

Anal. Calcd for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50. Found: C, 70.73; H, 10.58.

13,14,28,29-Tetraoxadispiro[11.2.12.2]nonacosane (12g)
Mp 202–204 °C ($CHCl_3$); R_f = 0.85 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.18–1.78 (m, 46 H, CH_2).

^{13}C NMR: δ = 22.4, 23.8, 24.3, 24.6, 24.8, 25.3, 25.8, 25.9, 26.3, 27.2, 27.9, 31.9, 111.4, 111.9.

Anal. Calcd for $C_{25}H_{46}O_4$: C, 73.12; H, 11.29. Found: C, 72.93; H, 11.19.

1-Nonyl-13,14,27,28-tetraoxadispiro[11.2.11.2]octacosane (12h)
Mp 205 °C ($CHCl_3$) with decomposition; R_f = 0.9 (TLC, Et_2O–petroleum ether, 1:1).

^{1}H NMR: δ = 0.84 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.14–1.78 (m, 59 H, CH, CH_2).

^{13}C NMR: δ = 14.7 (CH_3), 21.9–31.9 (30 C, CH, CH_2), 105.0, 106.2.

Anal. Calcd for $C_{33}H_{62}O_4$: C, 75.81; H, 11.95. Found: C, 75.63; H, 11.80.

3-Octyl-1,2,4,5-tetraoxaspiro[5.11]heptadecane (13a)
Mp 38–40 °C ($CHCl_3$); R_f = 0.8 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 0.84 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.13–1.72 (m, 36 H, CH_2), 4.71 (t, *J* = 5.9 Hz, 1 H, CH).

^{13}C NMR: δ = 14.0, 19.3, 21.8, 22.1, 22.4, 22.6, 24.1, 24.5, 24.7, 24.8, 25.2, 26.6, 29.7, 34.0, 107.8, 113.5.

Anal. Calcd for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31. Found: C, 70.61; H, 11.30.

3-Methyl-3-phenyl-1,2,4,5-tetraoxaspiro[5.11]heptadecane (13b)
Mp 95–97 °C ($CHCl_3$); R_f = 0.83 (TLC, Et_2O–petroleum ether, 1:4).

^{1}H NMR: δ = 1.21–1.84 (m, 25 H, CH_2, CH_3), 7.33–7.45 (m, 3 H, CH), 7.52–7.59 (m, 2 H, CH).

^{13}C NMR: δ = 19.4, 21.8, 22.3, 25.9, 26.0, 26.2, 29.7, 112.3, 115.3, 126.1, 126.5, 128.1, 128.2.

Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.69; H, 9.00.

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