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Nature Chooses Rings: Synthesis of Silicon-Containing Macrocyclic Peroxides

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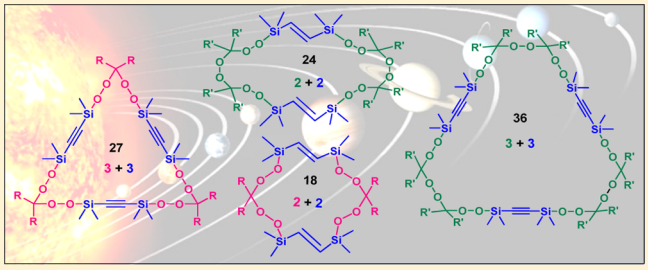
Supporting Information

ABSTRACT: The reactions of 1,2-bis(dimethylchlorosilyl)-ethane (**1**), 1,2-bis(dimethylchlorosilyl)ethene (**6**), and 1,2-bis(dimethylchlorosilyl)ethyne (**7**) with *gem*-bis-(hydroperoxides) **2a−h** and 1,1′-bis(hydroperoxy)bis-(cycloalkyl)peroxides **4a−c** were found to proceed in an unusual way. Thus, the reactions do not give the expected polymeric peroxides; instead, they produce cyclic silicon-containing peroxides containing 2, 4, or 6 silicon atoms in the ring: 9- (**3a−h**), 12- (**5a−c**), 18- (**8**, **12**), 24- (**9**, **10**), 27- (**13**), and 36-membered (**11**) compounds. The size of the rings produced in the reactions increases in the series 1,2-bis(dimethylchlorosilyl)ethane < 1,2-bis(dimethylchlorosilyl)ethene < 1,2-bis(dimethylchlorosilyl)ethyne. The resulting 9- and 12-membered cyclic peroxides are stable under ambient conditions. These compounds were isolated by chromatography and characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, X-ray diffraction, elemental analysis, and high-resolution mass spectrometry. The yields vary from 77 to 95%. Structures of the larger-size rings (18-, 24-, 27-, and 36-membered peroxides) were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy using 2D (COSY, HSQC, and HMBC), 2D DOSY ^{1}H, 3D ^{1}H−^{29}Si HMBC-DOSY NMR experiments, and elemental analysis.



INTRODUCTION

Organic peroxides belong to a class of compounds that are in considerable demand.[1] For more than 50 years, these compounds have been widely used in industry and scientific research as oxidants, autoxidation products, polymerization initiators, initiators in organic synthesis, cross-linking agents, and building blocks. In the past decades, organic peroxides, particularly those having a cyclic structure, have attracted interest as pharmaceutically active compounds. For example, some organic peroxides exhibit antimalarial,[2] antihelminthic,[3] or antitumor activity.[4] Peroxides with the Si−O−O fragment have similar applications and are used for the initiation of polymerization,[5] hydroxylation of arenes,[6] peroxidation,[7] thermal transformations,[8] and the synthesis of 1,2-dioxolanes,[9] 1,2-dioxanes,[9e,10] 1,2,4-trioxanes,[11] 1,2-dioxepanes,[9e] 1,2,4,5-tetraoxepanes,[12] and 1,2,4,5-tetraoxanes.[13] Silicon-containing peroxides are produced as intermediates in the Fleming[14] and Tamao−Kumada[15] oxidation. The fundamental aspects of the structures, properties, and reactivities of heteroorganic peroxides have drawn keen attention from researchers working in this field.[16]

On the whole, the chemistry of silicon-containing peroxides is less well developed in comparison to the chemistry of carbon-containing peroxides due, in part, to the shortage of selective methods for their synthesis. There are a limited number of routes to peroxides containing the Si−O−O fragment. These methods are based on the reactions of silyl

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triflates or chlorosilanes with hydroperoxides in the presence of bases,[7a,9a,b,17] singlet oxygen with silyl enolates,[18] compounds containing the Si−H bond with ozone,[19] hydroperoxides with *N*,*O*-bis(trimethylsilyl)acetamide,[20] and the $Co(L)_2/O_2/Et_3SiH$ system with unsaturated compounds.[21]

Advances in the chemistry of organosilicon peroxides have been considered in detail in reviews by Brandes and Blaschette,[22a] Aleksandrov,[22b] Tamao,[22c] Ando,[22d] Ricci,[22e] and Davies[22f] and in our review.[22g]

Only a few publications have been devoted to investigations on the chemistry of silicon-containing cyclic peroxides: in particular, on their synthesis. Thus, structures containing the endocyclic O−O−Si−O−O moiety were described: 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxa-3,6,9-trisilonane,[23] 1,2,4,5,7,8-hexaoxa-3-silonanes,[24] and some other related compounds.[22f,g,25] The scarcity of data on Si-containing cyclic peroxides is to a large extent associated with the fact that these compounds are synthesized using two bifunctional reagents, which easily form polymers. The synthesis of cyclic products of a given composition rather than oligomeric and polymeric products is a difficult or even intractable problem.

In the present study, we succeeded in selectively synthesizing 9- (**3a**−**h**), 12- (**5a**−**c**), 18- (**8**, **12**), 24- (**9**, **10**), 27- (**13**), and 36-membered (**11**) peroxides by the reactions of the following bifunctional reagents: *gem*-bis(hydroperoxides) **2a**−**h** and 1,1′-bis(hydroperoxy)bis(cycloalkyl)peroxides **4a**−**c** with 1,2-bis(dimethylchlorosilyl)ethane (**1**), 1,2-bis(dimethylchlorosilyl)ethene (**6**), and 1,2-bis(dimethylchlorosilyl)ethyne (**7**). It should be noted that 12-, 18-, 24-, 27-, and 36-membered peroxides containing the SiOOC moiety have been previously unknown. In organic chemistry, the approach to nine-membered and particularly to larger-ring compounds is always more difficult in comparison to the synthesis of 5−7-membered cyclic compounds. The synthesis of large-ring products is often accompanied by the formation of oligomers and sometimes requires special catalysts for the coupling of several molecules or high-dilution cyclization methods.[26] In addition, the approach to cyclic peroxides is complicated by the instability of the O−O group to some reagents used in organic synthesis.

RESULTS AND DISCUSSION

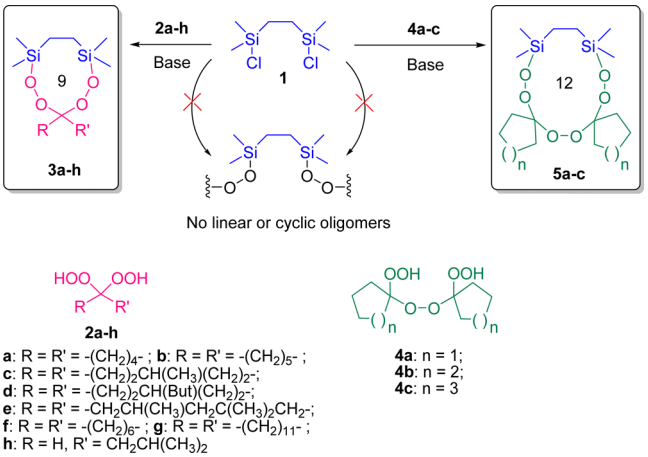
The present study consists of two parts. In the first part, we synthesized 9- and 12-membered peroxides and developed a general experimental procedure. In the second part, we synthesized 18-, 24-, 27-, and 36-membered peroxides.

Synthesis of Stable 9- and 12-Membered Peroxides. In the framework of the general strategy of the synthesis of 9- and 12-membered cyclic peroxides, we performed the reactions of *gem*-bis(hydroperoxides) **2a**−**h** and 1,1′-bis(hydroperoxy)-bis(cycloalkyl)peroxides **4a**−**c** with 1,2-bis-(dimethylchlorosilyl)ethane (**1**) (Scheme 1).

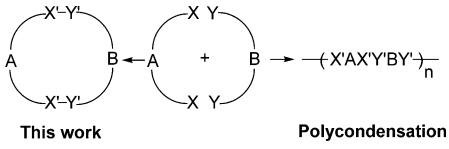
The work was performed in two stages. In the first stage, we examined the synthesis of 3-*tert*-butyl-9,9,12,12-tetramethyl-7,8,13,14-tetraoxa-9,12-disilaspiro[5.8]tetradecane (**3d**) starting from 1,2-bis(chlorodimethylsilyl)ethane (**1**) and 1,1-bis-(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**) and found the optimum reaction conditions. Then other 9- and 12-membered cyclic peroxides were synthesized, taking into account these conditions.

When proceeding to the synthesis of 9-membered peroxides, one cannot be sure that the result will be positive because structurally similar carbocycles are strained and, consequently, general methods for the construction of cyclic structures are often unsuitable for the synthesis of the latter compounds. In many instances, the synthesis of such compounds is accompanied by the formation of oligomers. It would be quite reasonable to expect that the reaction of two bifunctional reagents, geminal bis(hydroperoxides) **2a**−**h** and dichlorodisilane **1**, in which the Si−Cl groups are separated by three bonds, will lead to polycondensation. The latter process is observed in similar reactions: for example, in the synthesis of polyesters, polyamides, polycarbonates, polyurethanes, polyimides, and poly(ether sulfones)[27] (Scheme 2).

Scheme 1. Synthesis of 9- and 12-Membered Peroxides 3a−h and 5a−c by the Reactions of 1,2-Bis(dimethylchlorosilyl)ethane (1) with *gem*-Bis(hydroperoxides) 2a−h and 1,1′-Bis(hydroperoxy)bis(cycloalkyl)peroxides 4a−c, Respectively



Scheme 2



Earlier,[24] we successfully synthesized cyclic peroxides but in a more similar case. In dichlorosilanes used in our previous study, two chlorine atoms acting as leaving groups were attached to one silicon atom, whereas the large distance between chlorine atoms in the present study should promote the formation of polymers.[28]

To optimize the reaction conditions, we varied the nature of the base (amine) and the order of the addition of reagents in the reaction of bis(hydroperoxide) **2d** with dichlorodisilane **1**. We used aromatic and aliphatic bases, such as imidazole, pyridine, 2,6-dimethylpyridine, 4-dimethylaminopyridine, quinoline, tetrahydroquinoline, diethylamine, triethylamine, and DABCO. The yield of 1,2,7,8-tetraoxa-3,6-disilonane **3d** can be accurately determined due to a simple and reproducible procedure for the isolation and purification of this product (Table 1).

The highest yield of peroxide **3d** was obtained with the use of aromatic nitrogen-containing bases: 95% yield in the presence of imidazole (run 1) and somewhat lower yields (76, 65, and 64%) in the presence of 2,6-dimethylpyridine, DMAP, and pyridine, respectively (runs 3, 4, and 2). The aliphatic amines

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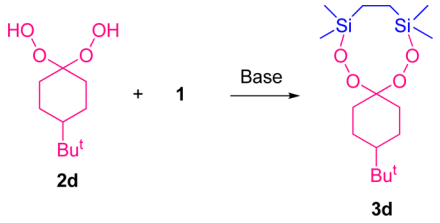
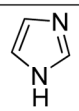
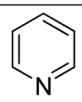
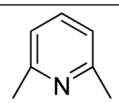
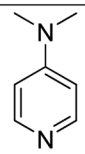
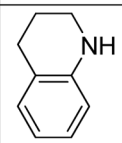
Table 1. Influence of the Nature of the Base and the Order of the Addition of Reagents on the Yield of Peroxide 3d in the Reaction of Bis(hydroperoxide) 2d with Dichlorodisilane 1[a]



Run	1	2	3	4	5	6	7	8	9
Base						Et_2NH	Et_3N	DABCO	In the absence of a base
Yield, %	95 14[b] 95[c]	64 64[b] 0[d]	76	65	0	26	57	15	0

[a]General procedure of the synthesis of peroxide **3d**: a solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) in Et_2O (2 mL) was added with stirring to a solution of bis(hydroperoxide) **2d** (0.109 g, 0.535 mmol) and amine (0.076−0.150 g, 1.123 mmol, 2.1 mol/mol of **2d**) in Et_2O (5 mL) at 20−25 °C for 2−3 min. The mixture was stirred for 1.5 h. Yields of **3d** are calculated as (mol of **3d**)/(mol of **2d**) × 100. [b]The order of mixing of reagents was changed: a solution of bis(hydroperoxide) **2d** (0.109 g, 0.535 mmol) in Et_2O (2 mL) was added with stirring to a solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) and amine (0.076−0.089 g, 1.123 mmol, 2.1 mol/mol of bis(hydroperoxide) **2d**) in Et_2O (5 mL) at 20−25 °C for 2−3 min. The mixture was stirred for 1.5 h. [c]The order of mixing of reagents was changed: a solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) and bis(hydroperoxide) **2d** (0.109 g, 0.535 mmol) in Et_2O (5 mL) was added with stirring to a solution of amine (0.076−0.089 g, 1.123 mmol, 2.1 mol/mol of bis(hydroperoxide) **2d**) in Et_2O (2 mL) at 20−25 °C for 2−3 min. The mixture was stirred for 1.5 h. [d]Pyridine was used as the reaction medium. Dichlorodisilane **1** (0.115 g, 0.535 mmol) was added with stirring to a solution of bis(hydroperoxide) **2d** (0.109 g, 0.535 mmol) in pyridine (5 mL) at 20−25 °C for 2−3 min. The mixture was stirred for 1.5 h.

(runs 5−8) Et_3N, Et_2NH, DABCO, and tetrahydroquinoline are less efficient than aromatic amines. In the absence of bases, product **3d** is not formed. The bases Et_2NH and tetrahydroquinoline react with bis(dimethylchlorosilyl)ethane and remove the latter from the reaction zone (runs 5 and 6).

In the presence of DABCO or Et_3N, a considerable amount of bis(hydroperoxide) **2d** decomposes to form 4-*tert*-butylcyclohexanone (runs 7 and 8). This observation was confirmed by NMR spectroscopy. The ^{13}C NMR spectrum recorded 20 min after the addition of a 2-fold molar excess of DABCO to a solution of bis(hydroperoxide) **2d** in $CDCl_3$ showed a signal at δ 212.4 corresponding to the carbonyl carbon atom of 4-*tert*-butylcyclohexanone.

The TLC monitoring showed no conversion of bis(hydroperoxide) **2d** and dichlorodisilane **1** in pyridine in run 2[d]. Apparently, dichlorodisilane **1** and bis(hydroperoxide) **2d** are solvated with pyridine, which hinders the reaction between the active centers of these reagents.

In the reaction, the base serves three main functions responsible for the yield of peroxide **3d.** First, the base increases the nucleophilicity of hydroperoxide by accepting an acidic proton. The second function is to react with chlorosilane. For example, the formation of stable complexes of amines with SiF_4 was documented.[29] In the present study, we observed a substantial difference in the yield of peroxide **3d** in the reactions with the use of imidazole and pyridine carried out according to two procedures, which are described in footnotes *a* and *b* of Table 1 to runs 1 and 2 and which differ in the order of the addition of reagents. According to footnote *a*(general procedure), dichlorodisilane **1** was added to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**) and amine, whereas 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**) was added to a solution of dichlorodisilane **1** and amine according to footnote *b* (runs 1 and 2). In run 1, the yields differ by more than a factor of 6, whereas in run 2 the yields remain unchanged. There is a substantial decrease in the yield with a change in the order of the addition of reagents in the reaction with imidazole (run 1), in contrast to the reactions with the use of pyridine (run 2), in which the unchanged yield is attributed to the formation of a complex stable to further transformations in run 1[b]. The existence of the latter complex was confirmed by NMR spectroscopy. In $CDCl_3$, the ^{13}C and ^{29}Si NMR spectra of dichlorodisilane **1** were recorded, and then the spectra of a mixture of **1** with imidazole (10−20 min after mixing) taken in molar ratios of 1:1, 1:2, 1:4, and 1:6 were measured. In the ^{13}C NMR spectra, the signals of the $SiCH_3$ and $SiCH_2$ groups, which are observed at δ 1.06 and 10.8, respectively, for dichlorodisilane **1**, are shifted to δ −0.128 and 9.7 (ratio 1:1), δ −1.203 and 8.667 (ratio 1:2), δ −3.042 and 7.055 (ratio 1:4), and δ −3.267 and 7.022 (ratio 1:6). In a mixture of dichlorodisilane **1** with pyridine, no shifts of ^{13}C NMR signals are observed.

In the ^{29}Si NMR spectrum of a mixture of dichlorodisilane **1** and imidazole, the signal of the silicon atom, which is observed at δ 32.88 for the starting dichlorodisilane **1**, is shifted to δ 28.1 (ratio 1:1), δ 24.6 (ratio 1:2), δ 18.85 (ratio 1:4), and δ 16.75 (ratio 1:6). The upfield shifts of the signals in the ^{13}C and ^{29}Si NMR spectra are apparently due to the formation of the five-coordinate complex in the reaction with the use of the reagents in a ratio of 1:1 or 1:2 and the formation of a six-coordinate complex with the use of a ratio of 1:4 or 1:6.[30a−c] It is also possible to suggest the formation of trisubstituted silyl imidazole in the case of 1:4 and 1:6 ratios on the basis of

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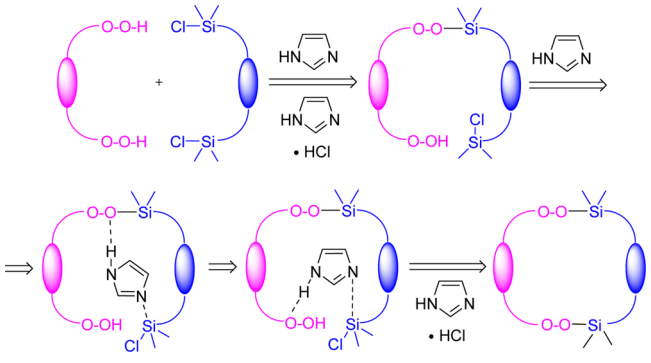
^{29}Si NMR spectral data.[30d−f] In the spectrum of a mixture of dichlorodisilane **1** and pyridine, the position of the ^{29}Si NMR signal remains virtually unchanged. In the reaction performed according to footnote *c* of Table 1 (run 1), a solution of dichlorodisilane **1** and bis(hydroperoxide) **2d** was added to a solution of amine, and peroxide **3d** was obtained in a yield equal to that obtained in the synthesis performed according to the general procedure. The third main function of amine is to bind hydrogen chloride that is eliminated and maintain a weakly acidic medium, which is of great importance for the reaction to proceed efficiently.

It was shown that the nature of the base is a key factor determining selectivity of cycle formation. The general cyclization mechanism was proposed on the basis of imidazole, which is the best base (Scheme 3).

Scheme 3. Possible Mechanism of Cycle Formation from Dichlorodisilanes and Dihydroperoxides with the Use of Imidazole as a Base



It can be proposed without getting into specifics that one Si−O bond is formed on the first stage. Then imidazole coordinates with a silicon atom and successively via a hydrogen atom with an oxygen atom of another peroxide group. This coordination envelops the molecule. Finally the second Si−O bond is formed with preparation of the peroxide cycle.

Then, to optimize the reaction conditions, we studied the influence of the nature of the solvent, the reaction time, and the imidazole:peroxide **2d**:dichlorodisilane **1** molar ratio on the yield of cyclic peroxide **3d** (Table 2).

Diethyl ether is the solvent of choice. Thus, in the time period from 0.1 to 29 h, the yield of peroxide **3d** varied in the range 41−95% (Table 2, runs 1−9); in runs 1 and 2 the reaction was not brought to completion, and in run 9 the target product was largely decomposed.

An excess amount of the base has little effect on the formation of peroxide **3d**. The reactions with the use of 2.1-, 4-, and 6-fold molar excesses of imidazole relative to bis(hydroperoxide) **2d** and dichlorodisilane **1** gave the target product in 95, 83, and 80% yields, respectively (Table 2, runs 3−5). The use of a 1.5-fold molar excess of dichlorodisilane **1** relative to bis(hydroperoxide) **2d** (run 6) led to a decrease in the yield of peroxide **3d** to 51%.

Solvents such as CH_3CN (Table 2, run 10) and CH_2Cl_2 (run 11) also proved to be efficient in this reaction; the reactions in THF gave the target product in lower yield (run 12).

It should be emphasized that the result depends on the rate of the addition of dichlorodisilane **1** to a mixture of bis(hydroperoxide) **2d** and imidazole. Thus, the rapid addition

Table 2. Influence of the Reaction Time, the Reagent Ratio, and the Nature of the Solvent on the Yield of Peroxide 3d in the Reaction of Bis(hydroperoxide) 2d with Dichlorodisilane 1 in the Presence of Imidazole as the Base[a]

run	time, h	solvent	molar ratio imidazole:**2d**:**1**	yield of **3d**, %
1	0.1	Et_2O	2.1:1:1	41
2	0.3	Et_2O	2.1:1:1	61
3	1.5	Et_2O	2.1:1:1	95
4	1.5	Et_2O	4:1:1	83
5	1.5	Et_2O	6:1:1	80
6	1.5	Et_2O	3.1:1:1.5	51
7	3	Et_2O	2.1:1:1	85
8	5	Et_2O	2.1:1:1	80
9	29	Et_2O	2.1:1:1	55
10	1.5	CH_3CN	2.1:1:1	70
11	1.5	CH_2Cl_2	2.1:1:1	72
12	1.5	THF	2.1:1:1	30

[a]General procedure of the synthesis of **3d**: a solution of dichlorodisilane **1** (0.115 or 0.173 g, 0.535 or 0.803 mmol) in Et_2O, CH_3CN, CH_2Cl_2, or THF (2 mL) was added with stirring to a solution of **2d** (0.109 g, 0.535 mmol) and imidazole (0.076−0.218 g, 1.123−3.210 mmol, 2.1−6 mol/mol of peroxide **2d**) in Et_2O, CH_3CN, CH_2Cl_2, or THF (5 mL) at 20−25 °C for 2−3 min. The reaction mixture was stirred for 0.1−29 h. Yields of **3d** are calculated as (mol of **3d**)/(mol of **2d**) × 100.

(over 1−2 s rather than for 2−3 min) results in the formation of an insoluble viscous white substance.

Peroxides **3a−h** were synthesized in Et_2O in 80−95% yields using a 2.1-fold molar excess of imidazole relative to bis(hydroperoxides) **2a−h** and dichlorodisilane **1** taken in equimolar amounts (Table 3).

Depending on the reactivity of geminal bis(hydroperoxides) **2a−h**, which decreases with increasing ring size, the reaction time was varied from 1 to 20 h with the aim of synthesizing **3a−h** in the highest yield. 1,1-Bis(hydroperoxy)-3,3,5-trimethylcyclohexane (**2e**) and 1,1-bis(hydroperoxy)cyclododecane (**2g**) appeared to be the least reactive. Thus, the reactions involving these compounds require 6.5 and 20 h, respectively, to be completed as opposed to 1−1.5 h needed for bis(hydroperoxides) **2a−d,f,h**. The relatively low yield of peroxide **3h** is, apparently, due to the low stability of the starting geminal bis(hydroperoxide) **2h** under the reaction conditions.

Determination of the Structures of 3a−h. The structures of **3a−h** were established on the basis of NMR spectroscopic data, taking into account the elemental analysis data. The ^{13}C NMR spectra show characteristic signals at δ 105.03−121.22 corresponding to the OOCOO moiety in related cyclic structures[24] and signals for the CH_2CH_2 (δ 4.61−4.96) and CH_3 (δ −3.5) groups. A significant feature is the change in the ^{29}Si NMR chemical shift, which is 32.9 ppm for dichlorodisilane **1** and 26.25 and 26.76 ppm for cyclic peroxide **3d**.

Since 1,2,4,5-tetraoxadisilonanes have been previously unknown, the formation of 18-membered peroxides as condensation products of four (2 + 2 coupling) rather than 2 molecules of the starting reagents cannot be ruled out. We studied the structures of **3d** (Figure 1) and **3g** by X-ray diffraction analysis and showed that these peroxides have a 9-membered cyclic structure.

Peroxides **3a−h** are stable during storage at 0 °C and can be purified by chromatography on silica gel. Peroxides **3a−c,e,f,h**

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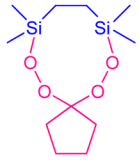
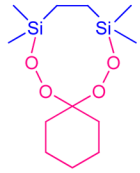
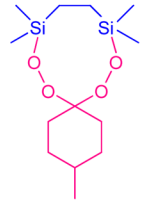
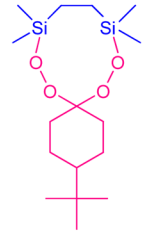
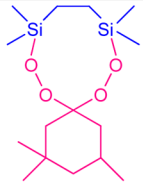
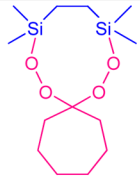
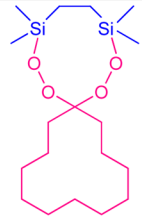
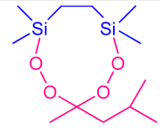
Table 3. Structures, Yields, and the Time of the Synthesis of 1,2,7,8-Tetraoxa-3,6-disilonanes 3a–h from *gem*-Bis(hydroperoxides) 2a–h and 1,2-Bis(dimethylchlorosilyl)ethane (1)[a]

Structures of 1,2,7,8-tetraoxa-3,6-disilonanes **3a-h**; yield, %; (reaction time, h)			
 **3a**; 85; (1.5)	 **3b**; 87; (1.5)	 **3c**; 95; (1)	 **3d**; 95; (1.5)
 **3e**; 93; (6.5)	 **3f**; 84; (1.5)	 **3g**; 94; (20)	 **3h**; 80; (1.5)

[a]General procedure of the synthesis of 1,2,7,8-tetraoxa-3,6-disilonanes **3a–h**: a solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) in Et_2O (2 mL) was added with stirring to a solution of bis(hydroperoxides) **2a–h** (0.148–0.200 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of **2a–h**) in Et_2O (5 mL) at 20–25 °C for 2–3 min. The solution was stirred for 1–20 h.

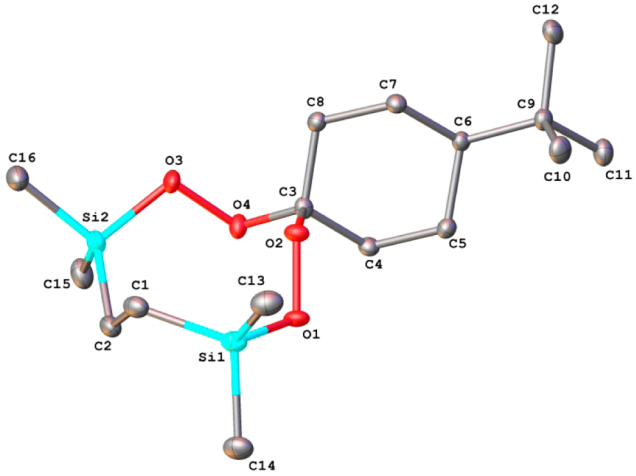


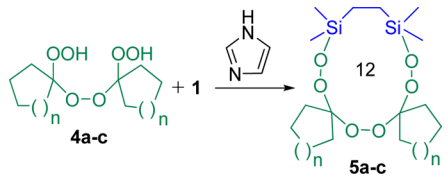
Figure 1. General view of molecule **3d** presented in ADP ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

are oily liquids, and peroxides **3d,g** are solids with melting points of 87–89 and 110–112 °C (without decomposition), respectively.

Synthesis of 12-Membered Cyclic Peroxides 5a–c from 1,1′-Bis(hydroperoxy)bis(cycloalkyl)peroxides 4a–c and 1,2-Bis(dimethylchlorosilyl)ethane (1). Twelve-membered cyclic compounds are difficult to synthesize, and they are poorly known in comparison to five- to seven-membered and even nine-membered cyclic compounds. Twelve-membered rings involving the SiOOC moiety are unknown, and only a few cyclic compounds containing the COOC moiety in such rings were described.[24]

When proceeding to the synthesis of 12-membered peroxides with the use of two bifunctional reagents, such as bis(hydroperoxy)bis(cycloalkyl)peroxides **4a–c** and dichlorodisilane **1**, in which the reaction centers are distant from each other, one would expect the predominant formation of oligomers or polymers.[27,28] However, we obtained 12-membered cyclic peroxides **5a–c** with good selectivity (Scheme 4).

Scheme 4. Synthesis of 1,2,7,8,10,11-Hexaoxa-3,6-disilacyclododecanes 5a–c from 1,1′-Bis(hydroperoxy)bis(cycloalkyl)peroxides 4a–c and 1,2-Bis(dimethylchlorosilyl)ethane (1)



Peroxides **5a–c** were synthesized in diethyl ether using a 2.1-fold molar excess of imidazole (Table 4).

The ring size (five-, six-, and seven-membered rings) in the starting dihydroperoxyperoxides **4a–c** has little effect on the results of the synthesis. Thus, peroxides **5a–c** were synthesized in 77–90% yields. Attempts to prepare 1,2,7,8,10,11-hexaoxa-3,6-disilacyclododecane using 1,1′-bis(hydroperoxy)bis(cyclododecyl)peroxide containing sterically hindered reaction centers failed even when the reaction time was increased to 24 h.

1,2,7,8,10,11-Hexaoxa-3,6-disilacyclododecanes **5a–c** show no clear evidence of decomposition during storage for 1 month at 0 °C. These compounds can be recrystallized from anhydrous solvents (MeOH and MeCN). Peroxides **5b,c** were found to have high melting points (113–116 and 124–126 °C (without decomposition), respectively).The structures of **5a–c** were determined by NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. The characteristic NMR signals at δ 109.1–121.0 correspond to the OOCOO moiety in related cyclic structures.[24] It is indicative that the ^{13}C NMR chemical shifts change on going from dichlorodisilane **1**

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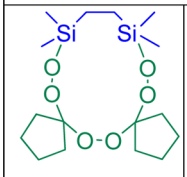
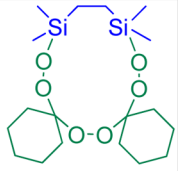
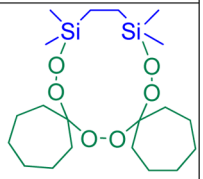
Table 4. Structures, Yields, and the Times of the Synthesis of 1,2,7,8,10,11-Hexaoxa-3,6-disilacyclododecanes 5a−c from 1,1′-Bis(hydroperoxy)bis(cycloalkyl)peroxides 4a−c and 1,2-Bis(dimethylchlorosilyl)ethane (1)[c]

Structures of 1,2,7,8,10,11-hexaoxa-3,6-disilacyclododecanes **5a-c**; yield, %.		
		
5a; 77[a], 40[b]	**5b**; 82[a], 46[b]	**5c**; 90[a], 56[b]

[a]Isolated by column chromatography. [b]Isolated by crystallization from MeOH. [c]General procedure of the synthesis of **5a−c**: a solution of dichlorodisilane **1** (0.150 g, 0.698 mmol) in Et_2O (1.5 mL) was added with stirring to a mixture of bis(hydroperoxy)peroxides **4a−c** (0.163−0.202 g, 0.698 mmol) and imidazole (0.1 g, 1.465 mmol, 2.1 mol/mol of peroxide **4a−c**) in Et_2O (3.5−4 mL) at 20−25 °C for 3−4 min. The reaction mixture was stirred for 3 h.

to 1,2,7,8,10,11-hexaoxa-3,6-disilacyclododecanes **5a−c** from 1.06 to −3.73 to −3.62 ppm for CH_3 and from 10.80 to 5.68−5.73 ppm for CH_2. The ^{29}Si NMR spectrum of dichlorodisilane **1** shows a signal at δ 32.88, whereas the corresponding signal in the spectrum of cyclic peroxide **5c** is observed at δ 27.5.

Since 1,2,7,8,10,11-hexaoxa-3,6-disilacyclododecanes have been previously unknown, the formation of 24-membered peroxides as condensation products of four (2 + 2 coupling) rather than two molecules of the starting reagents cannot be ruled out. It seemed to be important to directly confirm the structures of these compounds by X-ray diffraction analysis. For this purpose, we studied compound **5c** by X-ray diffraction (Figure 2).

The 11-membered ring adopts a crownlike conformation. It is worth noting that the presence of three peroxide groups does not lead to substantial changes in the bond lengths and bond angles in **5c** in comparison with those in **3d**,**g**.

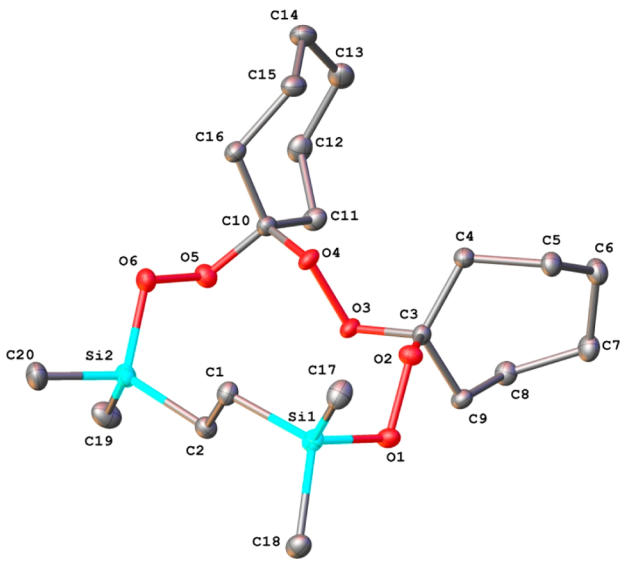


Figure 2. General view of molecule **5c** presented in ADP ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Synthesis and Analysis of 18- (8, 12), 24- (9, 10), 27- (13), and 36-Membered (11) Peroxides, Reaction Products of 1,2-Bis(dimethylchlorosilyl)ethene (6) and 1,2-Bis(dimethylchlorosilyl)ethyne (7) with *gem*-Bis-(hydroperoxide) 2d and 1,1′-Bis(hydroperoxy)peroxide 4c. Compounds containing 18-, 24-, 27-, or 36-membered rings are exceptionally rare among organic synthesis products because polymerization is often an insurmountable obstacle to their formation. In this part of the work, we performed the reactions of diperoxides **2d** and **4c** with the use of dichlorodisilanes[31] **6** and **7** having a double bond in the *E* configuration and a triple bond to synthesize silicon-containing macrocycles. The structural rigidity of dichlorodisilanes **6** and **7** should evidently preclude the ring formation by the coupling of two molecules; in this case the formation of oligomers seemed to be more likely. Instead, the reaction of **2d** or **4c** with 1,2-bis(dimethylchlorosilyl)ethene (**6**) gave cyclic peroxides **8** and **9** of a dimeric (2 + 2) composition, whereas the reaction with 1,2-bis(dimethylchlorosilyl)ethyne (**7**) produced cyclic peroxides **10** and **12** of a dimeric (2 + 2) composition and **11** and **13** of a trimeric (3 + 3) composition.

The structures of cyclic peroxides **8−13** were determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy using the 2D correlation techniques COSY, HSQC, and HMBC and by diffusion-ordered spectroscopy (DOSY), which allowed us to estimate the molecular weight and, as a consequence, the number of bis(hydroperoxide) and dichlorodisilane moieties in cyclic peroxides.

Diffusion-ordered spectroscopy is a very efficient tool for analyzing mixtures of compounds without their separation.[32] The diffusion coefficient for the molecule represented as a hard sphere is inversely proportional to six hydrodynamic radii of this sphere according to the Stokes−Einstein equation. On the assumption that there are no interactions between molecules of the dissolved compound and the solvent, the diffusion of molecules depends only on their molecular weight; consequently, diffusion coefficient measurements provide fairly accurate estimates of the molecular weights of dissolved compounds.[32]

The viscosity of the solvent $CDCl_3$ is insufficient to obtain high-quality interpretable DOSY NMR spectra. However, it was impossible to perform the reaction and record DOSY NMR spectra in commonly used, more viscous DMSO or D_2O because the peroxides in question are unstable in these solvents. To increase the viscosity of solutions in $CDCl_3$, we developed a method for recording DOSY NMR spectra by the addition of dry chemically inert nanosized silica gel (silica fume, powder, 14 nm particle size) to the solution under study in an amount of 1 wt %. It appeared that even small amounts of silica gel substantially increase the viscosity of the solution by converting it to gel, the spectral resolution remaining virtually unchanged. As a consequence, in the DOSY NMR spectra measured in the thickened solvent $CDCl_3$, individual components of the mixture are easily separated on the basis of the differing translation diffusion coefficients. In addition, the diffusion coefficients showed a logarithmic dependence on the molecular weight, thus providing a fairly accurate estimate of the molecular weights of the compounds in question.

The diffusion coefficients were measured by 2D DOSY ^{1}H NMR spectroscopy using the BPP-LED pulse sequence[33] in the presence of dibenzo-18-crown-6, pyridine, hexaoxononane (8,9,22,23,36,37-hexaoxatrispiro[6.2.11^{10}.2.11^{24}.2^7]-heptatriacontane),[34] and peroxides **3d** and **5c**, which are similar

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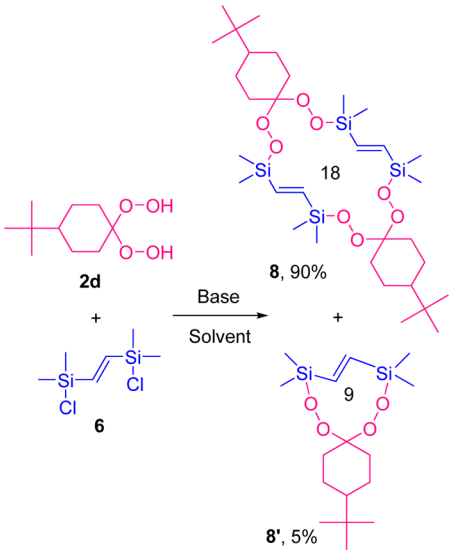
in the structure and polarity to the macrocyclic peroxides in question, as internal calibrants of known molecular masses. Since the chemical nature of these calibrants is similar to that of the compounds under study, their diffusion coefficients have a logarithmic dependence on the molecular weight, which was unambiguously established for the test specimen containing dibenzo-18-crown-6, hexaoxononane (8,9,22,23,36,37-hexaoxatrispiro[6.2.11^{10}.2.11^{24}.2^{7}]heptatriacontane), pyridine, and peroxides **3d** and **5c** with established structures.

Synthesis of 18-Membered Peroxide 8 from 1,2-Bis(dimethylchlorosilyl)ethene (6) and *gem*-Bis-(hydroperoxide) 2d. The synthesis of 18-membered peroxide **8** from 1,2-bis(dimethylchlorosilyl)ethene (**6**) and *gem*-bis-(hydroperoxide) **2d** was performed on a preparative scale in the presence of imidazole in Et_2O. The NMR spectra were measured in the presence of pyridine in $CDCl_3$ or $CDCl_3$ using silica fume for 2D DOSY ^{1}H NMR. Under these conditions, the reaction affords peroxide **8** as the major product along with trace amounts of nine-membered peroxide **8′** (Scheme 5).

Scheme 5. Synthesis of 8 from 1,2-Bis(dimethylchlorosilyl)ethene (6) and *gem*-Bis(hydroperoxide) 2d



Peroxide **8** was isolated in nearly quantitative yield (90%). In $CDCl_3$ and $CDCl_3$ with silica fume, peroxide **8** is stable for several days at temperatures below 0 °C.

The structure of peroxide **8** was unambiguously established by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy using the 2D correlation techniques COSY, HSQC, and HMBC and by diffusion-ordered spectroscopy (DOSY). A combination of 1D and 2D NMR techniques enabled us to determine the cyclic skeleton of the molecule, and the DOSY NMR data provided an estimate of its molecular weight and, consequently, the number of residual fragments of bis(peroxide) **2d** and dichlorodisilane **6** in molecule **8**.

On the basis of two 2D DOSY ^{1}H NMR spectra, it was found that peroxide **8** is a (2 + 2) dimer rather than the possible (1 + 1) monomer **8′** (Figures 3 and 4).

As can be seen from the 2D DOSY NMR spectrum (Figure 3), the diffusion coefficient of dimer **8** is smaller than the diffusion coefficient of dibenzo-18-crown-6 and, consequently, the molecular weight of peroxide **8** is higher than that of the crown ether. The diffusion coefficient of the monomeric compound **8′** should be larger than that of dibenzo-18-crown-6, which is unambiguously confirmed by the fact that the diffusion coefficient of the monomeric analogue **3d** is larger than that of dibenzo-18-crown-6 (Figure 4). The structure of **3d** has been established by X-ray diffraction analysis (vide supra). We recorded two 2D DOSY ^{1}H NMR spectra (Figures 3 and 4), which differ in that peroxide **3d** was added as the calibrant to the second sample (Figure 4), to avoid possible errors in the determination of the diffusion coefficients.

After the determination of the structure of the main compound **8**, the reaction mixture was analyzed by 3D ^{1}H–^{29}Si-HMBC-DOSY NMR spectroscopy for the presence of monomeric (**8′**) and trimeric peroxides. The 3D ^{1}H–^{29}Si-HMBC-DOSY spectrum was acquired using a new pulse sequence developed by us. In this approach, silicon is detected in the inverse mode, which substantially enhances the sensitivity of the method. On the basis of the 3D ^{1}H–^{29}Si-HMBC-DOSY NMR spectroscopic data (see the Supporting Information), it can be concluded that the mixture contains, in addition to the major dimeric peroxide **8**, a minor amount of the low-molecular-weight component, the monomeric peroxide **8′**.

Synthesis of 24-Membered Peroxide 9 from 1,2-Bis(dimethylchlorosilyl)ethene (6) and 1,1′-Bis-(hydroperoxy)bis(cycloheptyl)peroxide (4c). The preparative synthesis of 24-membered peroxide **9** was performed starting from 1,2-bis(dimethylchlorosilyl)ethene (**6**) and 1,1′-bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**) in the presence of imidazole in Et_2O. The NMR experiments were carried out in the presence of pyridine in $CDCl_3$ and $CDCl_3$ with silica fume for 2D DOSY ^{1}H NMR (Scheme 6).

This reaction affords peroxide **9** in 80% yield. The 24-membered dimeric structure of this compound was established by analogy with peroxide **8** on the basis of the ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data using 2D correlation techniques (COSY, HSQC, and HMBC) and DOSY NMR spectra (Supporting Information).

Synthesis of 24- (10) and 36-Membered (11) Peroxides from 1,2-Bis(dimethylchlorosilyl)ethyne (7) and 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c). The reaction of bis(dimethylchlorosilyl)ethyne (**7**) with 1,1′-bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**), giving a mixture of products, was carried out in the presence of imidazole in Et_2O. This reaction gives two macrocyclic peroxides: 24-membered dimeric peroxide **10** (30%) and 36-membered trimeric peroxide **11** (50%), as well as trace amounts (5%) of monomeric peroxide **10′**. The structure of **10′** was determined by X-ray diffraction (Scheme 7).

What is surprising is the fact that this reaction affords cyclic peroxides, which can be isolated from the reaction mixture, because the direct triple bond is an unsuitable fragment for the ring formation. Peroxides **10** and **11** are poorly stable. These compounds are less stable than 18-membered peroxide **8** and undergo spontaneous decomposition during storage in the reaction mixture in an NMR tube for 1–2 days, even at temperatures below 0 °C.

The structures of dimeric and trimeric peroxides **10** and **11** were established by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy using 2D correlation techniques (COSY, HSQC, and HMBC) and DOSY NMR spectroscopy, including the 3D ^{1}H–^{29}Si-HMBC-DOSY NMR spectra. The diffusion coefficients of these

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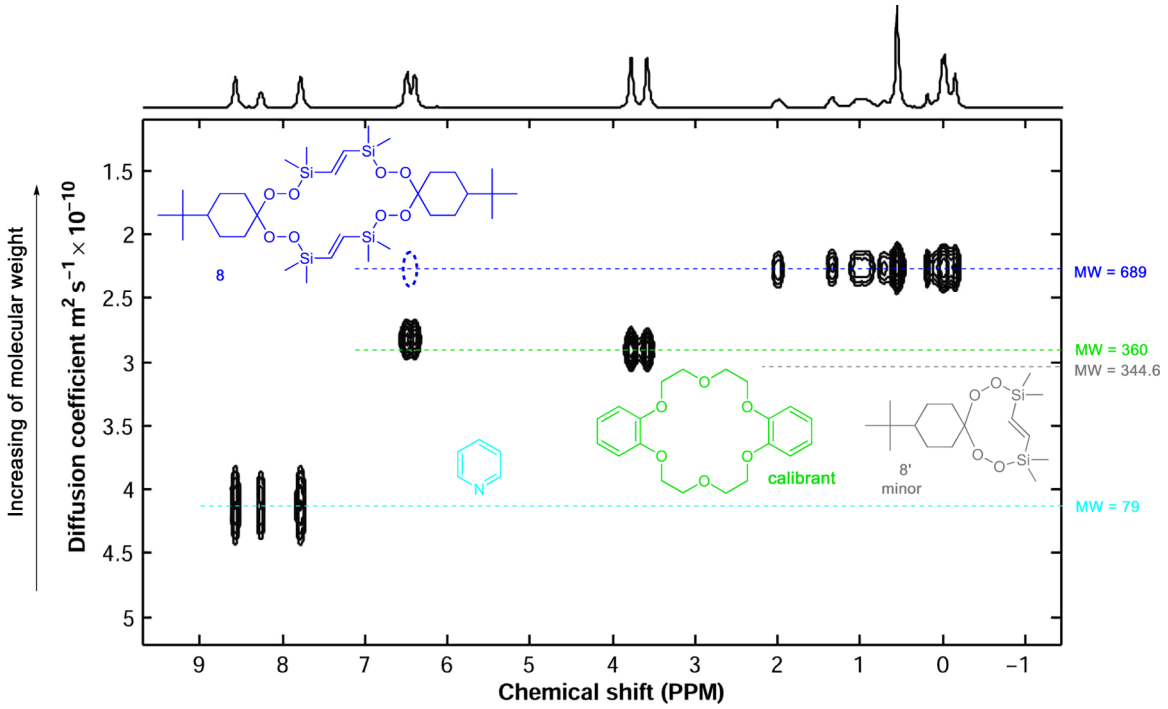

Figure 3. 2D DOSY ^{1}H NMR spectrum processed with the SCORE algorithm[35] for peroxide **8** using dibenzo-18-crown-6 as the calibrant.

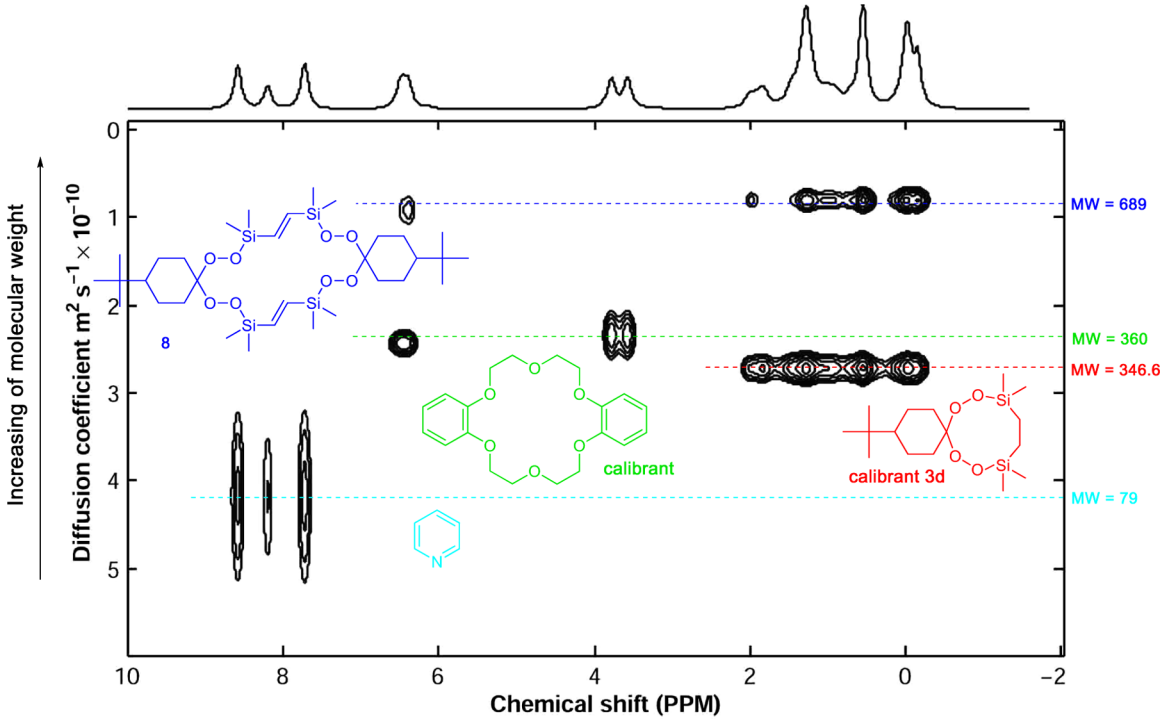

Figure 4. 2D DOSY ^{1}H NMR spectrum processed with the SCORE algorithm for peroxide **8** using dibenzo-18-crown-6 and **3d** as the calibrants.

compounds showed a logarithmic dependence on the molecular weight (Figure 5 and the Supporting Information).

The 2D DOSY ^{1}H NMR spectrum (Figure 5) shows that the diffusion coefficient of peroxide **10** is smaller than that of the crown ether (consequently, its molecular weight is higher than that of the crown ether), which is consistent with the molecular weight of dimeric peroxide. The smaller diffusion coefficient of peroxide **11** in comparison with that of peroxide **10** is evidence for the trimeric structure of **11**. Peaks of higher-molecular-weight oligomeric peroxides with the assumed diffusion coefficients (a brown dashed rectangle) are not observed.

Since dimeric and trimeric peroxides **10** and **11** have complex structures, we used 3D ^{1}H−^{29}Si-HMBC-DOSY NMR spectroscopy with the pulse sequence developed by us (see Figure 6; for more detail, see the Supporting Information) to exclude the possible error. According to this procedure, ^{29}Si atoms are detected in the inverse mode on the basis of protons, which substantially enhances the sensitivity of the method. The

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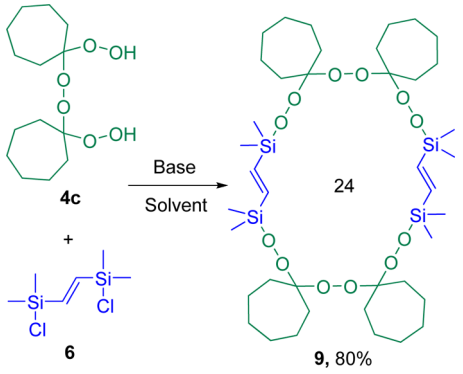
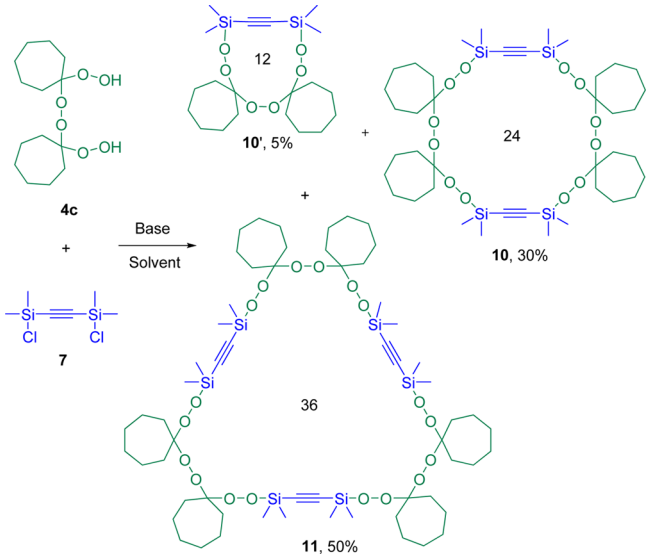
Scheme 6. Synthesis of Peroxide 9 from 1,2-Bis(dimethylchlorosilyl)ethene (6) and 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c)



Scheme 7. Synthesis of Peroxides 10′, 10, and 11 from 1,2-Bis(dimethylchlorosilyl)ethyne (7) and 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c)



addition of the third dimension in comparison with 2D spectra enables the separation of overlapping signals. The 3D $^{1}H-^{29}Si$-HMBC-DOSY NMR spectrum was recorded over 10−30 min. The applicability of the 3D $^{1}H-^{29}Si$-HMBC-DOSY NMR techniques for the purposes of the present study was examined using a test sample composed of silicon-containing peroxides **3d** and **5c** with established structures. The 3D ^{29}Si DOSY spectrum (Figure 6) ultimately confirms the structures of the peroxides. Thus, this spectrum shows two components with different diffusion coefficients corresponding to dimeric peroxide **10** and trimeric peroxide **11**.

Synthesis of 18- (12) and 27-Membered (13) Peroxides from 1,2-Bis(dimethylchlorosilyl)ethyne (7) and *gem*-Bis(hydroperoxide) 2d. The reaction of 1,2-bis(dimethylchlorosilyl)ethyne (7) with *gem*-bis(hydroperoxide) **2d** afforded a mixture of 9- (**12′**), 18- (**12**), and 27-membered (**13**) peroxides in 7, 32, and 40% yields, respectively (Scheme 8).

The structures of peroxides **12** and **13** were established by analogy with peroxides **10** and **11** by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy using 2D correlation techniques (COSY, HSQC, and HMBC) and DOSY NMR spectroscopy, including 3D $^{1}H-^{29}Si$-HMBC-DOSY NMR spectra.

Analysis of Peroxides 3d, 5c, and 8−13 on the Basis of ^{29}Si NMR Data. Along with DOSY NMR spectroscopy, the analysis of the chemical shifts in the ^{29}Si NMR spectra is a key point in the determination of the structures. These chemical shifts vary over a wide range and are strongly sensitive to the environment of the silicon atom, due to which the Si−O−O group can be ultimately identified in the molecular structure. To identify silicon-containing peroxides **8−13**, we used ^{29}Si NMR data. The chemical shifts in the ^{29}Si NMR spectra of **3d** and **5c** proved to be suitable as the reference values, because the structures of these compounds were determined by X-ray diffraction. The chemical shifts in the ^{29}Si NMR spectra of compounds **3d, 5c**, and **8−13**, which were synthesized in the present study, and in the spectra of dichlorodisilanes **1**, **6**, and **7** and their hydrolysis products (siloxanes) are given in Table 5.

Dichlorodisilanes **1**, **6**, and **7**, peroxides **3d**, **5c**, and **8−13**, and hydrolysis products of **1**, **6**, and **7**[28d] (siloxanes) have different chemical shifts in the ^{29}Si NMR spectra. In the series of each class of compounds, the signals are shifted upfield on going from the C−C to C≡C bond. Upfield shifts are observed also in the series chlorosilane−peroxysilane−siloxane.

CONCLUSIONS

We found a new phenomenon in the reactions of bifunctional chlorosilanes with diperoxide compounds, in which the cyclization dominates over polymerization. The nature of the base and the reaction conditions have a considerable effect on the selectivity of the ring formation.

The reactions of 1,2-bis(dimethylchlorosilyl)ethane (**1**) with *gem*-bis(hydroperoxides) **2a−h** and 1,1′-bis(hydroperoxy)bis(cycloalkyl)peroxides **4a−c** in the presence of bases produced the previously unknown classes of cyclic peroxides containing two silicon atoms in the ring: 9-membered 1,2,7,8-tetraoxa-3,6-disilonanes **3a−h** and 1,2,7,8,10,11-hexaoxa-3,6-disilacyclododecanes **5a−c** containing a 12-membered ring, which are uncommon in the chemistry of peroxides. Peroxides **3a−h** and **5a−c** are stable at 0 to −5 °C during storage for 3 months. These compounds were isolated by chromatography and recrystallization and were then characterized by NMR spectroscopy, mass spectrometry, X-ray diffraction, and elemental analysis. The yields of these products vary from 77 to 95% depending on the structural features.

The reactions of 1,2-bis(dimethylchlorosilyl)ethene and 1,2-bis(dimethylchlorosilyl)ethyne with *gem*-bis(hydroperoxide) **2d** and 1,1′-dihydroperoxyperoxide **4c** in the presence of bases afford the previously unknown 18- (**8**, **12**), 24- (**9**, **10**), 27- (**13**), and 36-membered (**11**) peroxides, whereas the expected polymeric peroxides are virtually not formed at all. The DOSY NMR spectroscopy proved to be a key method for structural investigations of silicon-containing peroxides. Peroxides **8−13** are stable at 0 to −5 °C during storage for 2 weeks.

The reactions of 1,2-bis(dimethylchlorosilyl)ethane, 1,2-bis(dimethylchlorosilyl)ethene, and 1,2-bis(dimethylchlorosilyl)ethyne give cyclic peroxides by the coupling of two, four, or six molecules, respectively. A decrease in the degree of freedom in chlorosilanes in going from 1,2-bis(dimethylchlorosilyl)ethane to 1,2-bis(dimethylchlorosilyl)ethyne directs the reaction to the formation of larger-size rings.

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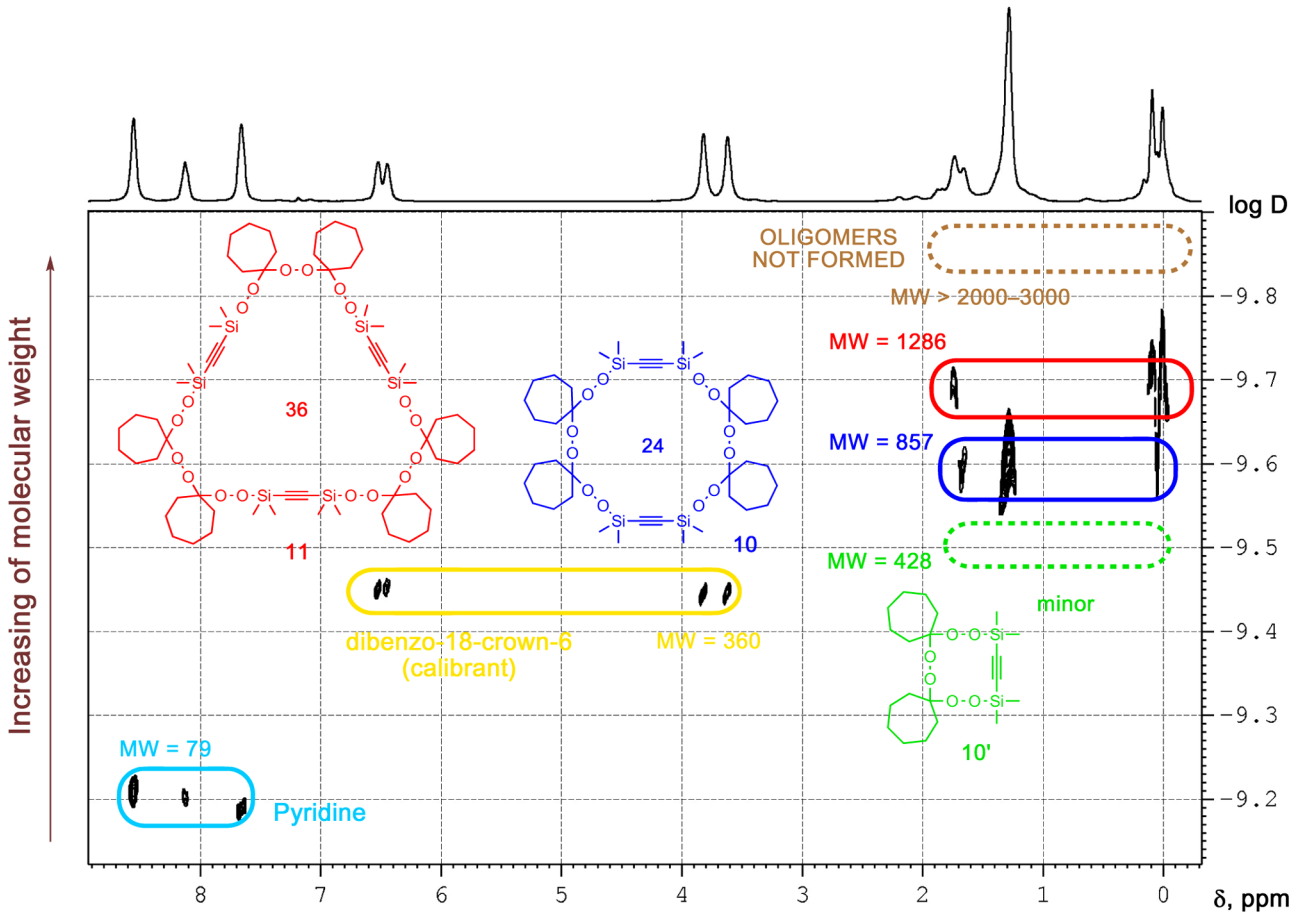

Figure 5. 2D DOSY ^{1}H NMR spectrum processed by the monoexponential fitting for peroxides **10** and **11** using dibenzo-18-crown-6 as the calibrant.

EXPERIMENTAL SECTION

General Experimental Details. *Caution!* We have encountered explosions in working with peroxides: precautions, such as the use of shields and fume hoods and the avoidance of transition-metal salts, heating, and shaking, should be taken whenever possible.

The ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz (400.1 and 100.6 MHz, respectively) and 300 MHz spectrometers (300.1 and 75.5 MHz, respectively) in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. The assignments of ^{1}H and ^{13}C NMR signals were made with the aid of 2D COSY, HSQC, and HMBC spectra where necessary. The ^{29}Si NMR spectra were recorded on a 300 MHz spectrometer (59.6 MHz; 300.1 MHz for ^{1}H) in $CDCl_3$ using the INEPT pulse sequence and Me_4Si as the standard. The assignments of ^{29}Si NMR signals were made with the aid of 2D HMBC spectra where necessary. Since it was impossible to directly detect some chemical shifts in the ^{29}Si NMR spectra, their values were taken from the corresponding 2D spectra. The reactions were monitored in NMR tubes in $CDCl_3$ solution containing 0.05% Me_4Si as the internal standard. The diffusion coefficients were measured using 2D DOSY ^{1}H NMR spectroscopy (diffusion ordered spectroscopy)[32] in $CDCl_3$ solution on a 300 MHz spectrometer (300.1 MHz for ^{1}H). The BPP-LED pulse sequence was used with Δ = 100 ms and T_e = 5 ms. The 2D DOSY NMR spectra were processed by the monoexponential fitting and SCORE algorithm using the Bruker TopSpin and DOSYToolbox software.[33] Dibenzo-18-crown-6 and peroxides **3d** and **5c**, which were added to the studied substances in a ∼1:1 molar ratio, served as the internal and external calibrants of known molecular masses in the DOSY NMR spectra. The 3D ^{1}H−^{29}Si HMBC-DOSY NMR spectra were acquired in $CDCl_3$ on a 300 MHz spectrometer (300.1 MHz for ^{1}H). The novel pulse sequence composed of BBP-LED and HMBC pulse sequences was used with Δ = 100 ms, T_e = 5 ms, and J_{SiH} = 6 Hz. The total experimental time varied from 10 to 30 min depending on the sample used. The 3D DOSY NMR spectra were processed by the monoexponential fitting of cross-peak volumes using the Bruker TopSpin software. Peroxides **3d** and **5c**, which were added to the studied substances in a ∼1:1 molar ratio, served as the internal and external calibrants of known molecular masses in the DOSY NMR spectra.

MeCN (HPLC grade) for ESI-HRMS experiments was ordered from Merck and used as supplied. All samples for ESI-HRMS experiments were prepared in 1.5 mL Eppendorf tubes. All plastic disposables (Eppendorf tubes and tips) used in sample preparation were washed with MeCN before use.

High-resolution mass spectra were recorded on a Bruker maXis instrument equipped with an electrospray ionization (ESI) ion source.[36] All measurements were performed in a positive (+MS) ion mode (interface capillary voltage 4500 V) with scan range m/z 50−3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for the all analyzed solutions in MeCN (flow rate 3 μL/min). Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L/min); the interface temperature was set at 180 °C. All spectra were processed by using the Bruker DataAnalysis 4.0 software package.

The TLC analysis was carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Chromatography was performed on silica gel (63−200 mesh and 5−40 μm).

CH_2Cl_2, Et_2O, petroleum ether (PE; 40/70), MeCN, THF, ethyl acetate, H_2O_2 (37% aqueous solution), cyclopentanone, cyclohexanone, 4-methylcyclohexanone, 4-*tert*-butylcyclohexanone, cycloheptanone, cyclododecanone, 4-methyl-2-pentanone, imidazole, pyridine, DMAP, 2,6-lutidine, tetrahydroquinoline, diethylamine, triethyl-

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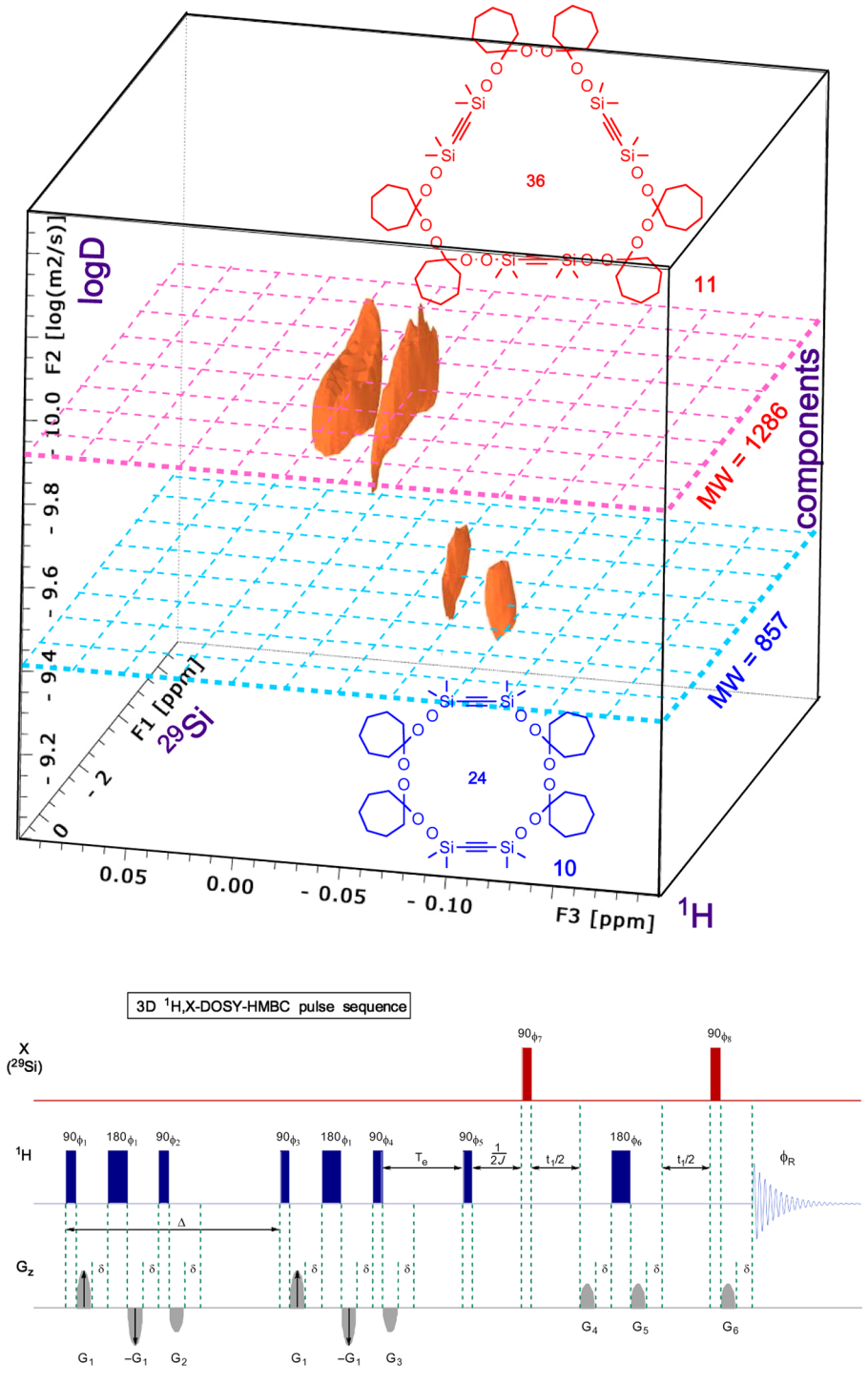

Figure 6. 3D $^{1}H-^{29}Si$-HMBC-DOSY NMR spectrum processed by the monoexponential fitting of cross-peak volumes for peroxides **10** and **11**.

amine, and DABCO were purchased from Acros. Silica fume (particle size 0.007 mm, S5130) was purchased from Sigma. A solution of H_2O_2 in Et_2O (5.8 wt %) was prepared by extraction with Et_2O (5 × 100 mL) from a 37% aqueous solution (100 mL) followed by drying over $MgSO_4$.

Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre: CCDC 992998 (**3d**), 992999 (**3g**), 993000 (**5c**), 993001 (**10′**).

1,2-Bis(chlorodimethylsilyl)ethane (1). This compound was purchased from Acros Organics. The ^{1}H and ^{13}C NMR spectroscopic data are similar to those reported in the study.[37] ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.42 (s, 12H), 0.81 (s, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 0.96, 10.70. ^{29}Si NMR (59.62 MHz, $CDCl_3$): δ 33.02.

***gem*-Bis(hydroperoxides) 2a–h.** These compounds were synthesized according to known procedures.[38]

*1,1-Bis(hydroperoxy)cyclopentane (**2a**).*[38] Oil. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.582.-2.05 (m, 8H), 9.80–10.05 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 24.4, 33.0, 122.1.

*1,1-Bis(hydroperoxy)cyclohexane (**2b**).*[38] Colorless crystals. Mp: 48–50 °C (Et_2O) (lit.[38] mp 48–49 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.32–1.61 (m, 6H), 1.72–1.91 (m, 4H), 9.45–9.65 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 22.3, 25.2, 29.4, 111.1.

*1,1-Bis(hydroperoxy)-4-methylcyclohexane (**2c**).*[38] Colorless crystals. Mp: 54–56 °C (Et_2O) (lit.[38] mp 53–55 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 0.92 (m, 3H), 1.1–1.71 (m, 7H), 2.11–2.29 (m,

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Scheme 8. Synthesis of Peroxides 12′, 12, and 13 from 1,2-Bis(dimethylchlorosilyl)ethyne (7) and *gem*-Bis(hydroperoxide) 2d

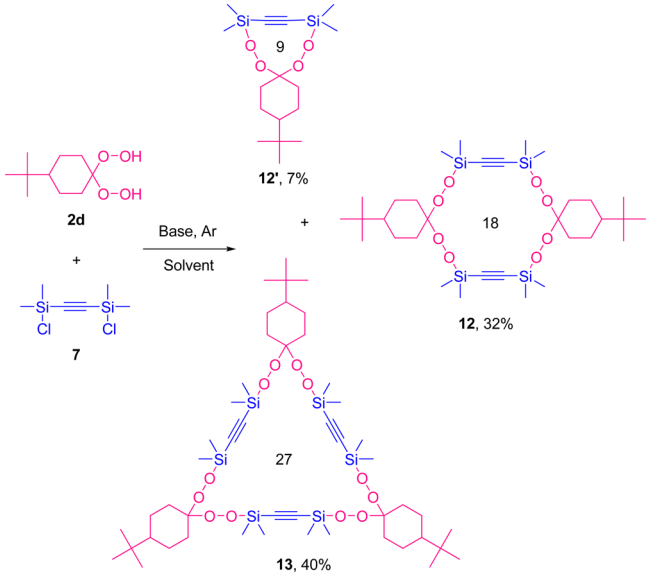
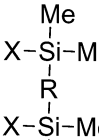


Table 5. ^{29}Si NMR Chemical Shifts (δ, ppm) for Dichlorodisilanes 1, 6, and 7, Si-Containing Peroxides 3d, 5c, and 8−13, and Siloxanes Synthesized by the Hydrolysis of 1, 6, and 7[a]

	R = $(CH_2–CH_2)$ (compound number)	R = (CH=CH) (compound number)	R = (C≡C) (compound number)
X = Cl	33 (**1**)	17 (**6**)	0 (**7**)
X = O-O-C	26÷27 (**3d, 5c**)	11÷14 (**8, 9**)	−1÷ −3 (**10-13**)
Hydrolysis products (siloxanes)	8	−4	−18

[a]The ^{29}Si NMR spectra were recorded using the INEPT pulse sequence and 2D HMBC techniques.

2H), 8.90−9.50 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 21.3, 29.0, 30.0, 31.5, 110.9.

*1,1-Bis(hydroperoxy)-4-tert-butylcyclohexane (**2d**).*[38] Colorless crystals. Mp: 81−83 °C (Et_2O) (lit.[38] mp 81−82.5 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 0.85 (s, 9H), 0.98−1.78 (m, 7H), 2.24−2.35 (m, 2H), 9.25−9.40 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 23.4, 27.6, 29.8, 32.3, 47.5, 110.7.

*1,1-Bis(hydroperoxy)-3,3,5-trimethylcyclohexane (**2e**).*[38] Colorless crystals. Mp: 55−57 °C (Et_2O) (lit.[38] mp 55.5−57 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 0.76−2.4 (m, 16H), 9.3−9.7 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 21.95, 25.3, 26.2, 31.39, 33.5, 37.5, 40.5, 48.1, 112.0.

*1,1-Bis(hydroperoxy)cycloheptane (**2f**).*[38] Colorless crystals. Mp: 20−21 °C (Et_2O) (lit.[38] mp 19−21 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.28−1.65 (m, 8H), 1.70−2.03 (m, 4H), 9.60−9.80 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 22.6, 29.7, 32.7, 115.7.

*1,1-Bis(hydroperoxy)cyclododecane (**2g**).*[38] Colorless crystals. Mp: 138−140 °C (Et_2O) (lit.[38] mp 138−140 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.21−1.82 (m, 22H), 9.98−10.04 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 20.0, 22.2, 22.5, 26.4, 26.5, 27.4, 113.

*2,2-Bis(hydroperoxy)-4-methylpentane (**2h**).*[38] Oil. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 0.96 (d, 6H, CH_3, J = 6.7 Hz), 1.42 (s, 3H, CH_3), 1.65−1.90 (m, 3H, CH_2, CH), 9.20−9.45 (br s, 2H, OOH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 17.9 (CH), 23.7, 24.2 (CH_3), 41.3 (CH_2), 112.7 (C).

1,1′-Bis(hydroperoxy)bis(cycloalkyl)peroxides 4a−c. These compounds were synthesized as has been described previously for **4a**,[39] **4b**,[39] **4c**,[39] and 1,1′-bis(hydroperoxy)bis(cyclododecyl)-peroxide.[39]

*1,1′-Bis(hydroperoxy)bis(cyclopentyl)peroxide (**4a**).* Colorless crystals. Mp: 60−62 °C (H_2O) (lit.[24a] mp 60−63 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.53−1.80 (m, 8H), 1.81−2.11 (m, 8H), 9.82−9.98 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$). δ: 23.5, 33.1, 122.1.

*1,1′-Bis(hydroperoxy)bis(cyclohexyl)peroxide (**4b**).* Colorless crystals. Mp: 80−82 °C (H_2O) (lit.[24a] mp 80−81 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.43−1.67 (m, 12H), 1.79−1.93 (m, 8H), 9.40−9.62 (br s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 22.8, 25.4, 29.9, 111.2.

*1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**).* Colorless crystals. Mp: 71−73 °C (H_2O) (lit.[24a] mp 71−72 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 1.51−1.71 (m, 16H), 1.93−2.04 (m, 8H), 9.57−9.65(s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 22.5, 29.8, 33.0, 116.2.

1,1′-Bis(hydroperoxy)bis(cyclododecyl)peroxide. Colorless crystals. Mp: 154−155 °C (Et_2O) (lit.[24a] mp 154−155.5 °C). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.21−1.82 (m, 44H), 9.78 (br s, 2H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 19.4, 21.9, 22.1, 25.9, 26.2, 26.4, 115.4.

Experiment Referred to Table 1: Synthesis of 3-*tert*-Butyl-9,9,12,12-tetramethyl-7,8,13,14-tetraoxa-9,12-disilaspiro[5.8]-tetradecane (3d). *Footnote a.* A solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring at 20−25 °C for 2−3 min to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) and, in runs 1−8, the corresponding amine: imidazole, pyridine, 2,6-dimethylpyridine, 4-dimethylaminopyridine, quinoline, tetrahydroquinoline, diethylamine, triethylamine, or DABCO (0.076−0.150 g, 1.123 mmol, 2.1 mol/mol of **2d**) in Et_2O (5 mL); in run 9, amine was not added. The mixture was stirred for 1.5 h. Petroleum ether (30 mL) was added to the reaction mixture, and the mixture was filtered through a short layer (1.5−2 cm) of silica gel (5−40 μm) using a water-jet vacuum pump. Then the solvent was evaporated using a water-jet vacuum pump.

Footnote b. A solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring at 20−25 °C for 2−3 min to a solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) and amine (imidazole in run 1 and pyridine in run 2; 0.076−0.089 g, 1.123 mmol, 2.1 mol/mol of peroxide **2d**) in Et_2O (5 mL). The mixture was stirred for 1.5 h. Compound **3d** was isolated as described in footnote *a*.

Footnote c, Run 2. Dichlorodisilane **1** (0.115 g, 0.535 mmol) was added with vigorous stirring at 20−25 °C for 2−3 min to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) in pyridine (5 mL). The mixture was stirred for 1.5 h. The TLC data and ^{1}H and ^{13}C NMR spectra showed no conversion of the starting reagents.

Footnote d. A solution of amine (0.076−0.089 g, 1.123 mmol, 2.1 mol/mol of peroxide **2d**) in Et_2O (2 mL) was added with stirring at 20−25 °C for 2−3 min to a solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) and 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) in Et_2O (5 mL). The mixture was stirred for 1.5 h. Compound **3d** was isolated as described in footnote *a*.

NMR Experiment on the Decomposition of 2d with DABCO and Et_3N. 1,1-Bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.025 g, 0.123 mmol) and DABCO (0.029 g, 0.257 mmol) or Et_3N (0.026 g, 0.123 mmol) were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. After storage for 20 min, ^{1}H and ^{13}C NMR spectra were recorded. In

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the ^{13}C NMR spectrum, a signal corresponding to the carbonyl carbon atom of 4-*tert*-butylcyclohexanone appeared at δ 212.4. The TLC data for the reaction mixture also confirmed the formation of 4-*tert*-butylcyclohexanone.

NMR Monitoring of the Reaction of 1,2-Bis-(dimethylchlorosilyl)ethane (1) with Imidazole in Different Ratios. Dichlorodisilane **1** (0.046 g, 0.214 mmol) and imidazole taken in molar ratios of 1:1 (0.0146 g, 0.214 mmol), 1:2 (0.029 g, 0.428 mmol), 1:4 (0.058 g, 0.856 mmol), and 1:6 (0.087 g, 1.284 mmol) were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. After storage for 20 min, the ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded. At the ratios **1**:imidazole = 1:1 and 1:2, the ^{29}Si NMR spectra were recorded also 24 h after mixing.

Experiment Referred to Table 2: Influence of the Reaction Time, the Reagent Ratio, and the Nature of the Solvent on the Synthesis of 3d from 2d in the Presence of Imidazole as the Base. General Procedure of the Synthesis of 3d. A solution of dichlorodisilane **1** (0.115 or 0.173 g, 0.535 or 0.803 mmol) in Et_2O, CH_3CN, CH_2Cl_2, or THF (2 mL) was added with vigorous stirring at 20−25 °C for 2−3 min to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) and imidazole (0.076−0.218 g, 1.123−3.210 mmol, 2.1−6 mol/mol of peroxide **2d**) in Et_2O, CH_3CN, CH_2Cl_2, or THF (5 mL). The mixture was stirred for 0.1−29 h.

The isolation was performed as described for **3d** (Table 1).

Experiment on the Effect of the Rate of the Addition of Bis(dimethylchlorosilyl)ethane (1) to a Mixture of 2d and Imidazole on the Synthesis of 3d. A solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring at 20−25 °C for 1−2 s to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of peroxide **2d**) in Et_2O (5 mL). An insoluble white viscous mixture was obtained.

Experiment Referred to Table 3. Synthesis of 1,2,7,8-Tetraoxa-3,6-disilonanes 3a−h. A solution of dichlorodisilane **1** (0.115 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring at 20−25 °C for 2−3 min to a solution of **2a−h** (0.148−0.200 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of **2a−h**) in Et_2O (5 mL). The mixture was stirred for 1−20 h. The isolation was performed as described for **3d** (Table 1).

*8,8,11,11-Tetramethyl-6,7,12,13-tetraoxa-8,11-disilaspiro[4.8]-tridecane (**3a**).* Oil. R_f = 0.57 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.15 (s, 12H), 0.80 (s, 4H), 1.22−2.07 (m, 8H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.48, 4.96, 24.83, 33.42, 121.22. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 26.7. Anal. Calcd for $C_{11}H_{24}O_4Si_2$: C, 47.79; H, 8.75; Si, 20.32. Found: C, 47.56; H, 8.74; Si, 20.45.

*9,9,12,12-Tetramethyl-7,8,13,14-tetraoxa-9,12-disilaspiro[5.8]-tetradecane (**3b**).* Oil. R_f = 0.79 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.14 (s, 12H), 0.78 (s, 4H), 1.23−1.86 (m, 10H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.48, 4.80, 22.76, 25.61, 30.07, 109.54. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 26.4. Anal. Calcd for $C_{12}H_{26}O_4Si_2$: C, 49.61; H, 9.02; Si, 19.34. Found: C, 49.55; H, 9.10; Si, 19.48.

*3,9,9,12,12-Pentamethyl-7,8,13,14-tetraoxa-9,12-disilaspiro[5.8]-tetradecane (**3c**).* Oil. R_f = 0.68 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.15 (s, 12H), 0.78 (s, 4H), 0.87−2.41 (m, 12H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.49, 4.79, 21.52, 29.56, 31.04, 31.80, 109.50. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 26.3, 26.7. Anal. Calcd for $C_{13}H_{28}O_4Si_2$: C, 51.27; H, 9.27; Si, 18.45. Found: C, 51.40; H, 9.28; Si, 18.62.

*3-tert-Butyl-9,9,12,12-tetramethyl-7,8,13,14-tetraoxa-9,12-disilaspiro[5.8]tetradecane (**3d**).* White crystals. Mp = 78−81 °C (MeOH). R_f = 0.81 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.14 (s, 12H), 0.78 (s, 4H), 0.84 (s, 9H), 0.89−2.4 (m, 9H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.48, 4.86, 23.64, 27.63, 30.25, 32.30, 47.51, 109.42. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 26.25, 26.8. Anal. Calcd for $C_{16}H_{34}O_4Si_2$: C, 55.44; H, 9.89; Si, 16.21. Found: C, 55.46; H, 9.77; Si, 16.35.

*2,2,4,9,9,12,12-Heptamethyl-7,8,13,14-tetraoxa-9,12-disilaspiro-[5.8]tetradecane (**3e**).* Oil. R_f = 0.57 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.10−0.20 (m, 12H), 0.66−2.36 (m, 20H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.86, −3.17, 4.61, 4.79, 22.09, 25.42, 26.35, 31.42, 33.68, 48.50, 110.74. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 25.9, 26.5. Anal. Calcd for $C_{15}H_{32}O_4Si_2$: C, 54.17; H, 9.70; Si, 16.89. Found: C, 54.16; H, 9.43; Si, 16.92.

*10,10,13,13-Tetramethyl-8,9,14,15-tetraoxa-10,13-disilaspiro-[6.8]pentadecane (**3f**).* Oil. R_f = 0.77 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.15 (s, 12H), 0.78 (s, 4H), 1.51−2.02 (m, 12H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.48, 4.92, 23.09, 30.17, 33.19, 105.03. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 24.8, 26.2. Anal. Calcd for $C_{13}H_{28}O_4Si_2$: C, 51.27; H, 9.27; Si, 18.45. Found: C, 51.40; H, 9.14; Si, 18.63.

*3,3,6,6-Tetramethyl-1,2,7,8-tetraoxa-3,6-disilaspiro[8.11]-eicosane (**3g**).* White crystals. Mp = 110−112 °C (MeOH). R_f = 0.9 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.14 (s, 12H), 0.78 (s, 4H), 1.3−1.74 (m, 22H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.48, 4.77, 19.56, 21.97, 22.32, 26.15, 26.70, 113.91. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 25.9. Anal. Calcd for $C_{18}H_{38}O_4Si_2$: C, 57.70; H, 10.22; Si, 14.99. Found: C, 57.92; H, 10.12; Si, 15.14.

*9-Isobutyl-3,3,6,6,9-pentamethyl-1,2,7,8,3,6-tetraoxadisilonane (**3h**).* Oil. R_f = 0.84 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.14 (s, 12H), 0.78 (s, 4H), 091−1.86(m, 12H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.52, 4.81, 18.44, 23.84, 24.40, 42.47, 111.36. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 26.4. Anal. Calcd for $C_{12}H_{28}O_4Si_2$: C, 49.27; H, 9.65; Si, 19.20. Found: C, 49.36; H, 9.70; Si, 16.32.

Experiment Referred to Table 4: Synthesis of 1,2,7,8,10,11-Hexaoxa-3,6-disilacyclododecanes 5a−c. General Procedure of the Synthesis of 5a−c. a solution of dichlorodisilane **1** (0.150 g, 0.698 mmol) in Et_2O (1.5 mL) was added with vigorous stirring at 20−25 °C for 3−4 min to a mixture of 1,1′-bis(hydroperoxy)bis-(cycloalkyl)peroxides **4a−c** (0.163−0.202 g, 0.698 mmol) and a base (0.1 g, 1.465 mmol) in Et_2O (3.5−4 mL). The mixture was stirred for 3 h.

Footnote a. Petroleum ether (30 mL) was added to the reaction mixture, and the mixture was filtered through a short layer (1.5−2 cm) of silica gel (5−40 μm) using a water-jet vacuum pump. Then the solvent was evaporated using a water-jet vacuum pump.

Footnote b. Petroleum ether (30 mL) was added, and the mixture was successively washed with a 5% NaOH solution (2 × 10 mL) and water (2 × 10 mL). The organic phase was separated and dried over $MgSO_4$. The solvent was evaporated using a water-jet vacuum pump. Products **5a−c** were isolated by crystallization from MeOH.

*15,15,18,18-Tetramethyl-6,7,13,14,19,20-hexaoxa-15,18-disiladispiro[4.2.4.8]eicosane (**5a**).* White crystals. Mp = 85−88 °C (MeOH). R_f = 0.7 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.14 (s, 12H), 0.85 (br s, 4H), 1.52−2.21 (m, 16H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.73, 5.68, 24.92, 33.97, 120.98. Anal. Calcd for $C_{16}H_{32}O_6Si_2$: C, 51.03; H, 8.56; Si, 14.92. Found: C, 50.83; H, 8.31; Si, 15.00. HRMS (ESI) m/z [M + Na]$^+$: calcd for $[C_{16}H_{32}NaO_6Si_2]^+$, 399.1630; found, 399.1629.

*17,17,20,20-Tetramethyl-7,8,15,16,21,22-hexaoxa-17,20-disiladispiro[5.2.5.8]docosane (**5b**).* White crystals. Mp = 113−116 °C (MeOH). R_f = 0.7 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.14 (s, 12H), 0.85 (br s, 4H), 1.14−2.23 (m, 20H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.62, 5.75, 22.70, 25.58, 30.60, 109.01. Anal. Calcd for $C_{18}H_{36}O_6Si_2$: C, 53.43; H, 8.97; Si, 13.88. Found: C, 53.18; H, 8.86; Si, 14.02. HRMS (ESI) m/z [M + Na]$^+$: calcd for $[C_{18}HH_{36}NaO_6Si_2]^+$, 427.1943; found, 427.1943.

*19,19,22,22-Tetramethyl-8,9,17,18,23,24-hexaoxa-19,22-disiladispiro[6.2.6.8]tetracosane (**5c**).* White crystals. Mp = 124−126 °C (MeOH). R_f = 0.75 (TLC, hexane−ethyl acetate, 10:1). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.13 (s, 12H), 0.85 (br s, 4H), 1.46−2.10 (m, 24H). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ −3.67, 5.73, 23.39, 31.07, 34.46, 115.04. Anal. Calcd for $C_{20}H_{40}O_6Si_2$: C, 55.52; H, 9.32; Si, 12.98. Found: C, 55.45; H, 9.23; Si, 12.83. HRMS (ESI) m/z [M + Na]$^+$: calcd for $[C_{20}H_{40}NaO_6Si_2]^+$, 455.2256; found, 455.2269.

Synthesis and Analysis of 18-Membered Peroxide 3,18-Di-*tert*-butyl-9,9,12,12,23,23,26,26-octamethyl-7,8,13,14,21,22,27,28-octaoxa-9,12,23,26-tetrasiladispiro-[5.8.5.8]octacosa-10,24-diene (8) from 1,2-Bis-

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(dimethylchlorosilyl)ethene (6) and *gem*-Bis(hydroperoxide) 2d. A solution of dichlorodisilane **6** (0.114 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring under argon at 20−25 °C for 2−3 min to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of **2d**) in Et_2O (5 mL). The mixture was stirred for 1.5 h. Petroleum ether (30 mL) was added to the reaction mixture, and the mixture was filtered through a short layer (1.5−2 cm) of silica gel (5−40 μm) using a water-jet vacuum pump. Then the solvent was evaporated using a water-jet vacuum pump. A mixture of peroxides **8** and **8′** was obtained in a total amount of 0.175 g. The yields of peroxides **8** and **8′** were approximately 90 and 5%, respectively (estimated from the 2D DOSY ^{1}H NMR spectrum).

Reaction of 1,2-Bis(dimethylchlorosilyl)ethene (6) with *gem*-Bis(hydroperoxide) 2d. Analysis of the Products on the Basis of ^{1}H, ^{13}C, ^{29}Si, COSY, HSQC, and HMBC NMR Data. 1,1-Bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.0352 g, 0.1724 mmol) and pyridine (0.0286 g, 0.362 mmol) taken in a molar ratio of 1:2.1 were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. The tube was purged with argon and then bis(chlorodimethylsilyl)ethene (**6**; 0.0367 g, 0.1724 mmol) was added. After 1 h, the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **8** and **8′** were recorded using 2D correlation techniques COSY, HSQC, and HMBC.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethene (6) with *gem*-Bis(hydroperoxide) 2d in the Presence of Dibenzo-18-crown-6 as the Calibrant. Analysis of the Products on the Basis of 2D DOSY ^{1}H NMR Data (Figure 3). The reaction was carried out as described above. After 1 h, dibenzo-18-crown-6 (0.0250 g, 0.0694 mmol) was added as the calibrant. Then silica fume (1 wt %) was added to the NMR tube, and the mixture was shaken. The 2D DOSY ^{1}H NMR spectrum was recorded. Conditions: $CDCl_3$, **8** 0.3 mol/L, 1 wt % silica fume, 32 °C, BPP-LED pulse sequence, Δ = 100 ms, T_e = 5 ms. The components in the spectrum are represented by horizontal dashed lines of different colors: **8**, blue; **8′**, gray (minor); dibenzo-18-crown-6, green; pyridine, light blue. The peak enclosed by a blue dashed oval is not observed upon the fitting due to overlap with more intense signals.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethene (6) with *gem*-Bis(hydroperoxide) 2d in the Presence of Dibenzo-18-crown-6 and Peroxide (3d) as Calibrants. Analysis of the Products on the Basis of 2D DOSY ^{1}H NMR Data (Figure 4). The reaction was carried out as described above. After 1 h, dibenzo-18-crown-6 (0.0250 g, 0.0694 mmol) and tetraoxadisilonate **3d** (0.0241 g, 0.0694 mmol) were added as the calibrants. Then silica fume (1 wt %) was added to the NMR tube, and the mixture was shaken. The 2D DOSY ^{1}H NMR spectrum was processed with the SCORE algorithm for peroxide using dibenzo-18-crown-6 and **3d** as the calibrants. Conditions: see Figure 3. The components in the spectra are represented by horizontal dashed lines of different colors: **8**, blue; **3d**, red; dibenzo-18-crown-6, green; pyridine, light blue.

*3,18-Di-tert-butyl-9,9,12,12,23,23,26,26-octamethyl-7,8,13,14,21,22,27,28-octaoxa-9,12,23,26-tetrasiladispiro[5.8.5.8]-octacosa-10,24-diene (**8**, Major) and 3-tert-Butyl-9,9,12,12-tetramethyl-7,8,13,14-tetraoxa-9,12-disiladispiro[5.8]tetradec-10-ene (**8′**, Minor).* R_f = 0.88 (TLC, hexane−ethyl acetate, 10:1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.2−0.45 (m, 24H, 12H), 0.8−2.4 (m, 36H, 18H), 6.65−6.95 (m, 4H, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −2.6 (br), 22.7, 23.7, 27.7, 30.6, 32.3, 47.6, 109.3, 149.1. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 12.7, 13.5. Anal. Calcd for $C_{32}H_{64}O_8Si_4$: C, 55.77; H, 9.36; Si, 16.30. Found: C, 54.32; H, 9.78; Si, 15.79.

Synthesis and Analysis of 24-Membered Peroxide 19,19,22,22,43,43,46,46-Octamethyl-8,9,17,18,23,24,32,33,41,42,47,48-dodecaoxa-19,22,43,46-tetrasilatetraspiro[6.2.6^{10}.8.6^{25}.2.6^{34}.8^7]octatetraconta-20,44-diene (9) from 1,2-Bis(dimethylchlorosilyl)ethene (6) and 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c). A solution of bis(chlorodimethylsilyl)ethylene (**6**; 0.114 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring under argon at 20−25 °C for 2−3 min to a solution of 1,1′-bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**; 0.155 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of **4c**) in Et_2O (5 mL). The mixture was stirred for 1.5 h. Then petroleum ether (30 mL) was added, and the reaction mixture was filtered through a short layer (1.5−2 cm) of silica gel (5−40 μm) using a water-jet vacuum pump. Then the solvent was evaporated using a water-jet vacuum pump. Product **9** was synthesized in 80% yield (0.184 g, 0.214 mmol).

Reaction of 1,2-Bis(dimethylchlorosilyl)ethene (6) with 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c). Analysis of the Products on the Basis of ^{1}H, ^{13}C, ^{29}Si, COSY, HSQC, and HMBC NMR Data. 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**; 0.05 g, 0.1724 mmol) and pyridine (0.0286 g, 0.362 mmol) taken in a molar ratio of 1:2.1 were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. The tube was purged with argon, and then bis(chlorodimethylsilyl)ethylene (**6**; 0.0367 g, 0.1724 mmol) was added. After storage for 1 h, ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded using 2D correlation techniques COSY, HSQC, and HMBC.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethene (6) with 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c) in the Presence of Dibenzo-18-crown-6 as the Calibrant. Analysis of the Products on the Basis of 2D DOSY ^{1}H NMR Data. The reaction was performed as described above. After 1 h, dibenzo-18-crown-6 (0.0250 g, 0.0694 mmol) was added as the calibrant. Then silica fume (1 wt %) was added to the NMR tube, and the mixture was shaken. The 2D DOSY ^{1}H NMR spectrum was recorded.

*19,19,22,22,43,43,46,46-Octamethyl-8,9,17,18,23,24,32,33,41,42,47,48-dodecaoxa-19,22,43,46-tetrasilatetraspiro[6.2.6^{10}.8.6^{25}.2.6^{34}.8^7]octatetraconta-20,44-diene (**9**).* R_f = 0.7 (TLC, hexane−ethyl acetate, 10:1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.1−0.6 (m, 24H), 1.3−2.2 (m, 48H), 6.7−6.8 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −3.5 (br), 23.1, 30.8, 34.4, 115.5, 148.6. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 11.6, 12.65. Anal. Calcd for $C_{40}H_{76}O_{12}Si_4$: C, 55.78; H, 8.89; Si, 13.04. Found: C, 54.23; H, 9.01; Si, 12.36.

Synthesis and Analysis of 24- and 36-Membered Peroxides 19,19,22,22,43,43,46,46-Octamethyl-8,9,17,18,23,24,32,33,41,42,47,48-dodecaoxa-19,22,43,46-tetrasilatetraspiro[6.2.6^{10}.8.6^{25}.2.6^{34}.8^7]octatetraconta-20,44-diyne (10) and 19,19,22,22,43,43,46,46,67,67,70,70-dodecamethyl-8,9,17,18,23,24,32,33,41,42,47,48,56,57,65,66,71,72-octadecaoxa-19,22,43,46,67,70-hexasilahexaspiro-[6.2.6^{10}.8.6^{25}.2.6^{34}.8.6^{49}.2.6^{58}.8^7]doheptaconta-20,44,68-triyne (11) from 1,2-Bis(dimethylchlorosilyl)ethyne (7) and 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c). A solution of dichlorodisilane **7** (0.113 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring under argon at 20−25 °C for 2−3 min to a solution of 1,1′-bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**; 0.155 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of **4c**) in Et_2O (5 mL). Then petroleum ether (30 mL) was added, and the reaction mixture was filtered through a short layer (1.5−2 cm) of silica gel (5−40 μm) using a water-jet vacuum pump. Then the solvent was evaporated using a water-jet vacuum pump. A mixture of peroxides **10**, **10′**, and **11** was obtained in a total amount of 0.195 g. The yields of peroxides **10**, **10′**, and **11** were approximately 30, 5, and 50%, respectively (2D DOSY ^{1}H NMR spectroscopic data).

Reaction of 1,2-Bis(dimethylchlorosilyl)ethyne (7) with 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c). Analysis of the Products on the Basis of ^{1}H, ^{13}C, ^{29}Si, COSY, HSQC, and HMBC NMR Data. 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (**4c**; 0.05 g, 0.1724 mmol) and pyridine (0.0286 g, 0.362 mmol) taken in a molar ratio of 1:2.1 were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. The tube was purged with argon, and then bis(chlorodimethylsilyl)ethyne (**7**; 0.0364 g, 0.1724 mmol) was added. After storage for 1 h, ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded using 2D correlation techniques COSY, HSQC, and HMBC.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethyne (7) with 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c) in the Presence of Dibenzo-18-crown-6 as the calibrant. Analysis of the Products on the Basis of 2D DOSY ^{1}H NMR Data (Figure 5). The reaction was performed as described above. After 1 h, dibenzo-18-crown-6 (0.025 g, 0.0694 mmol) was added as the calibrant. Then silica fume (1 wt %) was added to the NMR tube, and the mixture was shaken. The 2D DOSY ^{1}H NMR spectrum was processed by the monoexponential fitting for peroxides **10** and **11** using dibenzo-18-crown-6 as the calibrant. Conditions: $CDCl_3$, see Figure 3. The major

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compounds in the spectrum are indicated by a solid triangle; possible and minor compounds are represented by dashed triangles of different colors: **10**, blue; **11**, red; dibenzo-18-crown-6, yellow; **10′** (minor; its peaks are observed upon strong enhancement of the signal intensity in the spectrum), green; oligomeric peroxides (not observed), brown; pyridine, light blue.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethyne (7) with 1,1′-Bis(hydroperoxy)bis(cycloheptyl)peroxide (4c). Analysis of the Products on the Basis of 3D ^{1}H−^{29}Si-HMBC-DOSY NMR Data (Figure 6). The reaction was performed as described above. After 1 h, silica fume (1 wt %) was added to the NMR tube, and the mixture was shaken. The 3D ^{1}H−^{29}Si-HMBC-DOSY NMR spectrum was processed by the monoexponential fitting of cross-peak volumes for peroxides **10** and **11**. Conditions: $CDCl_3$, 0.3 mol/L, 1 wt % silica fume, 32 °C. Pulse sequence: Δ = 100 ms, T_e = 5 ms, $J_{Si,H}$ = 6 Hz. The top of Figure 6 gives a 3D view of the HMBC-DOSY data; the methyl region of the products is shown. The components in the spectra are represented by horizontal dashed planes of different colors: **10**, blue; **11**, red. The bottom of Figure 6gives the 3D HMBC-DOSY pulse sequence. This pulse sequence is constructed of BPP-LED and HMBC sequences. The narrow and wide filled rectangles represent 90 and 180° pulses (dark blue for the ^{1}H channel, dark red for the ^{29}Si channel), and gray solid half-ellipses are *z*-gradient pulses. Vertical arrows indicate diffusion-encoding gradient pulses, which are incremented in sympathy, and half-ellipses without arrows are homospoil-type gradients. Delays: Δ is the diffusion time, T_e is the eddy current delay, δ is the gradient recovery delay. Gradient ratios: G_1 = 0−100%, diffusion-encoding gradient pulses; G_2 = −17.13%; G_3 = −13.17%; G_4 = 50−70%; G_5 = 20−30%; $G_6 = (G_4 + G_5)/(\gamma_H/\gamma_X) + (G_4 - G_5)$. Phases: ϕ_1 = 0; ϕ_2 = 0; ϕ_3 = 0; ϕ_4 = 0; ϕ_5 = 0; ϕ_6 = 0022; ϕ_7 = 02; ϕ_8 = 00002222; ϕ_R = 02022020.

*19,19,22,22,43,43,46,46-Octamethyl-8,9,17,18,23,24,32,33,41,42,47,48-dodecaoxa-19,22,43,46-tetrasilatetraspiro[6.2.6^{10}.8.6^{25}.2.6^{34}.8^{7}]octatetraconta-20,44-diyne (**10**, Major), 19,19,22,22,43,43,46,46,67,67,70,70-Dodecamethyl-8,9,17,18,23,24,32,33,41,42,47,48,56,57,65,66,71,72-octadecaoxa-19,22,43,46,67,70-hexasilahexaspiro-[6.2.6^{10}.8.6^{25}.2.6^{34}.8.6^{49}.2.6^{58}.8^{7}]doheptaconta-20,44,68-triyne (**11**, Major), and 19,19,22,22-Tetramethyl-8,9,17,18,23,24-hexaoxa-19,22-disiladispiro[6.2.6.8]tetracos-20-yne (**10′**, minor).* R_f = 0.61 (TLC, hexane−ethyl acetate, 10:1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.2−0.45 (m, 24H, 36H, 12H), 1.35−2.2 (m, 48H, 72H, 24H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −1.5 (br), 22.65 (br), 30.5(br), 33.1(br), 114.8, 138.6. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −2.7 Anal. Calcd for $C_{40}H_{72}O_{12}Si_4$, $C_{60}H_{108}O_{24}Si_6$: C, 56.04; H, 8.46; Si, 13.10. Found: C, 55.97; H, 8.83; Si, 13.16.

Synthesis and Analysis of 18- and 27-Membered Peroxides 3,18-Di-*tert*-butyl-9,9,12,12,23,23,26,26-octamethyl-7,8,13,14,21,22,27,28-octaoxa-9,12,23,26-tetrasiladispiro-[5.8.5.8]octacosa-10,24-diyne (12) and 3,18,32-Tri-*tert*-butyl-9,9,12,12,23,23,26,26,37,37,40,40-dodecamethyl-7,8,13,14,21,22,27,28,35,36,41,42-dodecaoxa-9,12,23,26,37,40-hexasilatrispiro[5.8.5^{15}.8.5^{29}.8^{6}]dotetraconta-10,24,38-triyne (13) from 1,2-Bis(dimethylchlorosilyl)ethyne (7) and *gem*-Bis(hydroperoxide) 2d. A solution of dichlorodisilane **7** (0.113 g, 0.535 mmol) in Et_2O (2 mL) was added with vigorous stirring under argon at 20−25 °C for 2−3 min to a solution of 1,1-bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.109 g, 0.535 mmol) and imidazole (0.076 g, 1.123 mmol, 2.1 mol/mol of **2d**) in Et_2O (5 mL). Petroleum ether (30 mL) was added, and the reaction mixture was filtered through a short layer (1.5−2 cm) of silica gel (5−40 μm) using a water-jet vacuum pump. Then the solvent was evaporated using a water-jet vacuum pump. A mixture of peroxides **12, 12′**, and **13** was obtained in a total amount of 0.145 g. The yields of peroxides **12, 12′**, and **13** were approximately 32, 7, and 40%, respectively (2D DOSY ^{1}H NMR spectroscopic data).

Reaction of 1,2-Bis(dimethylchlorosilyl)ethyne (7) with *gem*-Bis(hydroperoxide) 2d. Analysis of the products on the Basis of ^{1}H, ^{13}C, ^{29}Si, COSY, HSQC, and HMBC NMR Data. 1,1-Bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.0352 g, 0.1724 mmol) and pyridine (0.0286 g, 0.362 mmol) taken in a molar ratio of 1:2.1 were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. The tube was purged with argon, and then bis(chlorodimethylsilyl)ethyne (**7**; 0.0364 g, 0.1724 mmol) was added. After 1 h, ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded using 2D correlation techniques COSY, HSQC, and HMBC.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethyne (7) with *gem*-Bis(hydroperoxide) 2d in the Presence of Dibenzo-18-crown-6 as the Calibrant. Analysis of the Products on the Basis of 2D DOSY ^{1}H NMR Data. The reaction was performed as described above. Then silica fume (1 wt %) was added to the NMR tube, and the mixture was shaken. The 2D DOSY ^{1}H NMR spectrum was recorded.

Reaction of 1,2-Bis(dimethylchlorosilyl)ethyne (7) with *gem*-Bis(hydroperoxide) 2d. Analysis of the Products on the Basis of 3D ^{1}H−^{29}Si-HMBC-DOSY Data. 1,1-Bis(hydroperoxy)-4-*tert*-butylcyclohexane (**2d**; 0.0352 g, 0.1724 mmol) and pyridine (0.0286 g, 0.362 mmol) taken in a molar ratio of 1:2.1 were dissolved in $CDCl_3$ (0.6 mL) in an NMR tube. The tube was purged with argon, and then bis(chlorodimethylsilyl)ethyne (**7**; 0.0364 g, 0.1724 mmol) was added. After 1 h, silica fume (1 wt %) was added to the tube, and the mixture was shaken. The 3D ^{1}H−^{29}Si-HMBC-DOSY spectrum was recorded.

*3,18-Di-tert-butyl-9,9,12,12,23,23,26,26-octamethyl-7,8,13,14,21,22,27,28-octaoxa-9,12,23,26-tetrasiladispiro[5.8.5.8]-octacosa-10,24-diyne (**12**. Major), 3,18,32-Tri-tert-butyl-9,9,12,12,23,23,26,26,37,37,40,40-dodecamethyl-7,8,13,14,21,22,27,28,35,36,41,42-dodecaoxa-9,12,23,26,37,40-hexasilatrispiro[5.8.5^{15}.8.5^{29}.8^{6}]dotetraconta-10,24,38-triyne (**13**, Major), and 3-tert-Butyl-9,9,12,12-tetramethyl-7,8,13,14-tetraoxa-9,12-disilaspiro[5.8]tetradec-10-yne (**12′**, Minor).* R_f = 0.76 (TLC, hexane−ethyl acetate, 10:1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.25−0.45 (m, 24H, 36H, 12H), 0.8−2.45 (m, 36H, 54H, 18H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −1.38 (br), 23.6, 27.7, 30.6, 32.5, 47.7, 109.6, 139.4. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ −2.5, −2.0. Anal. Calcd for $C_{32}H_{60}O_8Si_4$, $C_{48}H_{90}O_{12}Si_6$: C, 56.10; H, 8.83; Si, 16.40. Found: C, 55.95; H, 9.02; Si, 15.67.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving ^{1}H, ^{13}C, 2D, and 3D NMR spectra, mass spectra, and details of X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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