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Synthesis of Cyclic Peroxides Containing the Si-*gem*-bisperoxide Fragment. 1,2,4,5,7,8-Hexaoxa-3-silonanes as a New Class of Peroxides

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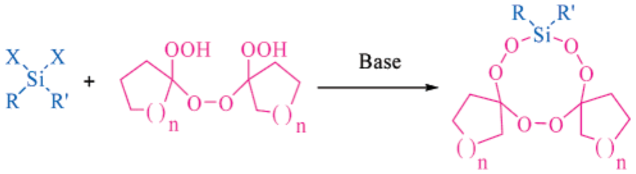
Received December 21, 2007



Stable peroxides
21 Examples, 59-96 %

A method was developed for the synthesis of the previously unknown class of organic peroxides, 1,2,4,5,7,8-hexaoxa-3-silonanes, based on the reaction of dialkyldichlorosilanes with 1,1′-dihydroperoxyperoxides. 1,2,4,5,7,8-Hexaoxa-3-silonanes are rather stable under ambient conditions and were characterized by NMR spectroscopy, X-ray diffraction, and elemental analysis. Their yields are in a range of 59−96%. The attempts were made to prepare 1,2,4,5-tetraoxa-3-silinanes by the reaction of dialkyldichlorosilanes with *gem*-bishydroperoxides. 1,2,4,5-Tetraoxa-3-silinanes were detected by NMR spectroscopy; these compounds rapidly decompose upon isolation.

Introduction

Organic peroxides belong to a broad and highly demanded class of compounds.[1] These compounds have found wide application in industrial and laboratory synthesis as oxidants, polymerization initiators, cross-linking agents, building blocks, intermediates in autoxidation, and substances having antimalarial and antimicrobial activities. Peroxides containing the $\mathrm{Si-O-O}$ fragment have similar applications. They are used primarily for the polymerization initiation,[2] hydroxylation of arenes,[3] peroxidation,[4] and in thermal transformations.[5] These compounds are produced as intermediates in the Fleming[6] or Tamao−Kumada[7] oxidation: conversion of alkyl silanes to alcohols by means of peracids or hydrogen peroxide. However, the chemistry of organosilicon peroxides is less well-known due, in part, to the fact that the methods of their synthesis are few in number. There are several routes to peroxides containing the $\mathrm{Si-O-O}$ fragment. These methods are based on the reactions of chlo-

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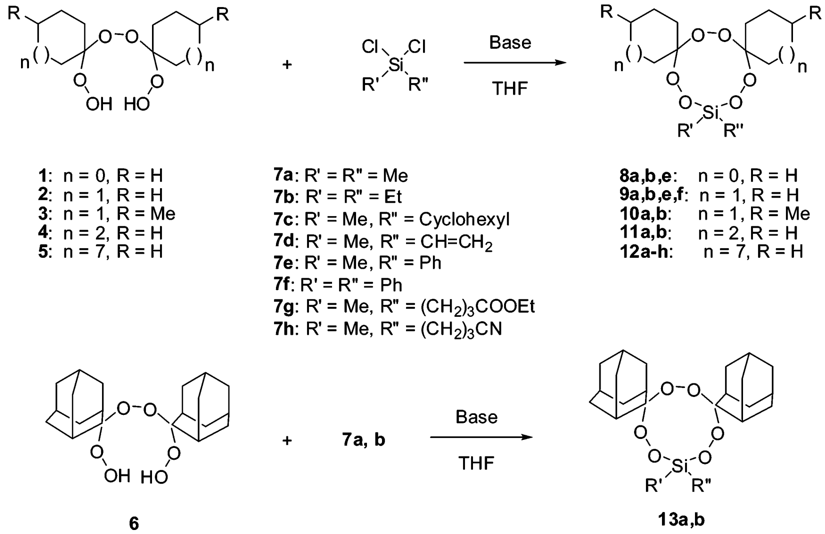
10.1021/jo7027213 CCC: $40.75

SCHEME 1. Synthesis of 1,2,4,5,7,8-hexaoxa-3-silonanes



rosilanes with hydroperoxides in the presence of bases,[8] singlet oxygen with silyl enolates,[9] compounds containing the Si−H bond with ozone,[10] hydroperoxides with *N,O*-bis(trimethylsilyl)-acetamide,[11] and the $Co(L)_2/O_2/Et_3SiH$ system with unsaturated compounds.[12] Mono-, di-, tri-, and tetraperoxy-substituted silanes have been synthesized according to these methods.

Some aspects of the chemistry of organosilicon peroxides have been reviewed by Brandes and Blaschette,[13a] Aleksandrov,[13b] Tamao,[13c] Ando,[13d] Ricci,[13e] and Davies.[13f] An analysis of the published data shows that no systematic studies of the properties and reactions of cyclic peroxides containing the O−O−Si−O−O fragment have been performed, and efficient procedures for the synthesis of these compounds are lacking. Only a few structures containing the O−O−Si−O−O fragment in the ring (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxa-3,6,9-trisilonane[14a] and 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetraoxa-3-silonane[14b]) were documented.

Results and Discussion

The aims of the present study were to examine the possibility of the existence of 1,2,4,5-tetraoxa-3-silinanes and 1,2,4,5,7,8-hexaoxa-3-silonanes, which belong to new classes of cyclic di- and triperoxides containing one Si atom and two or three O−O bonds in the ring, under ambient conditions, develop an approach to the synthesis of such compounds, evaluate their stability during isolation and storage, and characterize these compounds by NMR spectroscopy. In addition, the goal was to estimate to what extent the formation of oligomeric (linear) peroxides competes with the cyclization.

The reactions of *gem*-bishydroperoxides and 1,1′-dihydroperoxyperoxides with available dialkyldichlorosilanes and standard procedures for the isolation and identification of the products were used as the general strategy for the synthesis of the target peroxides.

Synthesis of 1,2,4,5,7,8-Hexaoxa-3-silonanes. Initially, we examined the synthesis of 1,2,4,5,7,8-hexaoxa-3-silonanes (**8**−**13**) based on the condensation of 1,1′-dihydroperoxyperoxides (**1**−**6**) with dialkyldichlorosilanes (**7a**−**h**) in the presence of bases (Scheme 1).

When we proceeded to the synthesis of peroxides **8**−**13** containing a nine-membered ring, we could not be quite sure

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TABLE 1. Synthesis of Hexaoxasilonane 12a from Me_2SiCl_2 7a[a] and 1,1′-Dihydroperoxyperoxide 5 in the Presence of Different Bases

base	pyridine	DMAP	quinoline	imidazole	Et_3N	DABCO	DBU	in the absence of bases
ratio, mole of base per mole of **5**	5	5	5	5 (3; 7)	5	4	5	
reaction time, h	3	3 (1)	3 (1; 17)	3	3	3	3 (1)	3
yield **12a**,[b] %	83 (85[c])	94 (71)	94 (70; 94)	96 (93; 96)	21	34	5 (traces)	5

[a] A one-and-a-half molar excess of Me_2SiCl_2 **7a** with respect to **5**. [b] Yield based on the isolated product. [c] A 6-fold molar excess of Me_2SiCl_2 **7a** with respect to **5**.

that the goal would be attained. It is known that general methods for the construction of structurally similar carbocycles containing a nine-membered ring are not always applicable to the synthesis of such carbocycles because of the formation of oligomers.

The procedure for the synthesis of peroxide **12a** was optimized and the influence of the reaction conditions on the yield of the target compound was studied on the basis of the reaction of dichlorodimethylsilane **7a** with dihydroperoxyperoxide **5**. We used the following aromatic and aliphatic nitrogen bases: pyridine, DMAP, quinoline, imidazole, DABCO, DBU, and triethylamine.

In this reaction, the base serves several functions. First, it increases the nucleophilicity of hydroperoxide groups via proton abstraction from dihydroperoxide. This is evident from the results of NMR experiments. The ^{1}H and ^{13}C NMR spectra of dihydroperoxyperoxide **2** and its mixture with imidazole in a molar ratio of 1:2 were recorded in $CDCl_3$. In the ^{1}H NMR spectrum of the mixture, the signal for the protons of the OOH groups of compound **2** (at δ 9.5) disappeared. In the ^{13}C NMR spectrum, the signal for the quaternary carbon atom was shifted upfield (from δ 111.1 to δ 110).

The second function of amine in this reaction is, apparently, to form complexes with dialkyldichlorosilane. For example, the formation of stable complexes in the reactions of amines with SiF_4 was documented.[15] The mixing of Me_2SiCl_2 with imidazole affords a precipitate, and the reaction of the latter with dihydroperoxyperoxide **5** produces 1,2,4,5,7,8-hexaoxa-3-silonane **12a** in 71% yield.

In addition, nitrogen bases serve as acceptors of hydrogen chloride that is eliminated in the course of the reaction. It is important to trap hydrogen chloride and maintain the basicity of the medium. If these conditions are not fulfilled, 1,2,4,5,7,8-hexaoxa-3-silonanes undergo decomposition.

The yield of peroxides depends, among other things, on the nature of the base. The influence of this factor and other reaction conditions was examined for the synthesis of peroxide **12a** which is characterized by high stability. The easy and reproducible procedure for the purification and isolation of peroxide **12a** allowed the precise determination of its yield (Table 1).

The highest yield of peroxide **12a** was achieved in the reactions of **5** and **7a** with use of aromatic nitrogen-containing bases. Peroxide **12a** was prepared in virtually quantitative yield (94 and 96%) in the presence of DMAP, quinoline, or imidazole; in somewhat lower yield (83%), in the presence of pyridine.

An excess amount of a base has little effect on the formation of peroxide **12a**. In the presence of a 3-, 5-, or 7-fold molar excess of imidazole with respect to dihydroperoxyperoxide **5**, the yield of the target product was 93, 96, and 96%, respectively. An increase in the excess of dichlorosilane **7a** from 1.5- to 6-fold had virtually no effect on the yield of peroxide **12a**. The reaction time required for the achievement of the best result in the presence of DMAP or quinoline is 3 h. A decrease in the reaction time from 3 to 1 h leads to a decrease in the yield of peroxide **12a** from 94 to ca. 70%.

As can be seen from Table 1, aliphatic amines, Et_3N, DABCO, and DBU are less efficient than aromatic amines. In the presence of DABCO, dihydroperoxyperoxide **5** is decomposed to a considerable extent to give cyclododecanone as the major product, whereas peroxide **12a** is produced in a yield of only 34%.

The low efficiency of triethylamine may be a consequence of the partial decomposition of peroxide **12a**. An analogous effect has been observed earlier [2a] in the reaction of dimethylamine with peroxides containing the Si−O−O−C fragment. The formation of **12a** is not catalyzed by DBU, and dihydroperoxyperoxide **5** remains virtually unconsumed. In the absence of bases, compound **12a** is produced in a yield of only 5%.

It can be assumed that the main difference in the yields of **12a** with the use of aliphatic and aromatic amines results from the specific character of their complexation with dihydroperoxyperoxide **5**. Contrary to aromatic amines, aliphatic amines form complexes with dihydroperoxyperoxide **5** of low reactivity, which either decompose or react slowly with silane **7a.**

Peroxides **8**−**13** were synthesized with the use of a 3-fold molar excess of imidazole; silanes **7a**−**h**, with a 1.2-fold molar excess with respect to dihydroperoxyperoxides **1**−**5**. Under these conditions, peroxides **8**−**13** were isolated in high preparative yields (59−94%, see Table 2).

Under these conditions, the reaction is completed in from 1 to 24 h depending on the structures of the starting reagents, primarily, on the volume of the substituents R′ and R″ at the silicon atom in dichlorosilanes **7a**−**h**. As expected, the condensation of peroxides **1**−**5** with sterically unhindered dichlorodimethylsilane **7a** proceeds most easily; the reaction with dichlorodiethylsilane **7b** proceeds somewhat less readily. The rate of the reaction with dichlorodiphenylsilane **7f** sharply decreases; however, this reaction also produces peroxides **9f** and **12f** in satisfactory yields (78−79%). An insignificant amount of phenol was detected among the reaction products in the condensation of peroxides **2** and **5** with dichlorodiphenylsilane **7f**.

The ring size in peroxides **1**−**5** also influences the results of the reaction, although to a lesser extent than the structures of the substitutes R′ and R″ in dialkyldichlorosilanes **7a**−**h**.

Unexpectedly, in contradiction with the steric factor, the yield of peroxide **12a** containing the 12-memebred ring appeared to be higher than that of peroxide **8a** containing the five-membered ring. Most likely, this difference is attributed to the partial hydrolysis of peroxide **8a** in the course of chromatographic purification on silica gel. This conclusion is consistent with the quantitative results of the hydrolysis of hexaoxasilonanes presented in Table 3.

Diacetoxydimethylsilane can also be used for the cyclization, as was exemplified by the synthesis of **8a**, **9a**, **11a**, and **12a**. These reactions produce peroxides in lower yields compared

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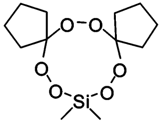
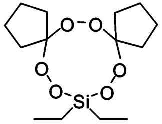
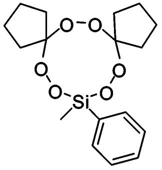
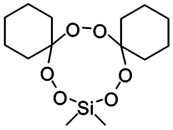
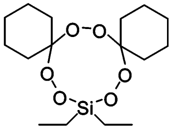
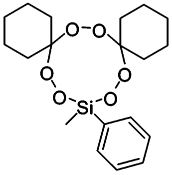
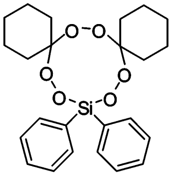
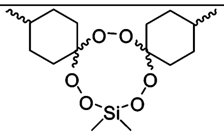
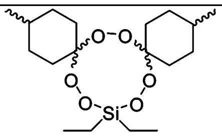
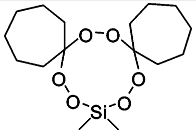
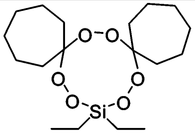
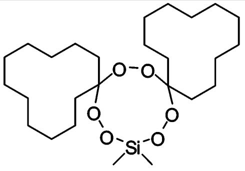
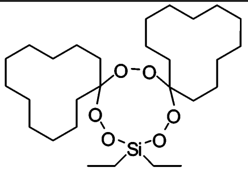
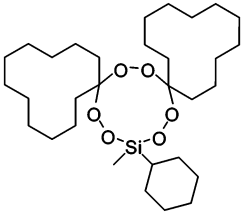
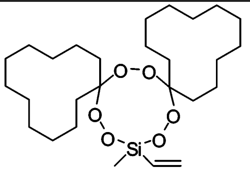
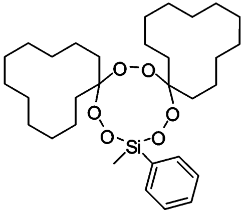
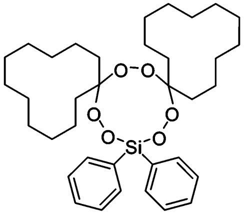
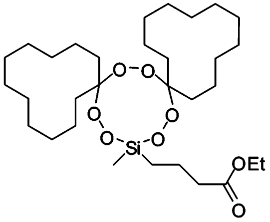
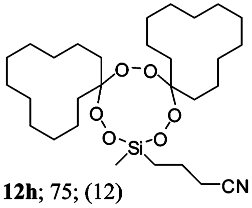
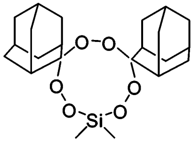
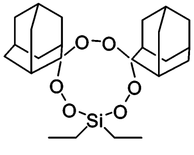
TABLE 2. Synthesis of 1,2,4,5,7,8-Hexaoxa-3-silonanes 8−13

Structures of 1,2,4,5,7,8,3-hexaoxasilonanes **8-13**; yield, % ^{a} ; (reaction time, h)		
 **8a**; 77; 61^{b}; (1)	 **8b**; 85; (3)	 **8e**; 75; (3)
 **9a**; 76; 64^{b}; (1)	 **9b**; 88; (3)	 **9e**; 83; (3)
 **9f**; 79; (8)	 **10a**; 76; (1)	 **10b**; 88; (3)
 **11a**; 77; 59^{b}; (1)	 **11b**; 86; (3)	 **12a**; 94; 73^{b}; (3)
 **12b**; 92; (12)	 **12c**; 83; (12)	 **12d**; 88; (12)
 **12e**; 82; (12)	 **12f**; 78; (24)	 **12g**; 81; (12)
 **12h**; 75; (12)	 **13a**; 83; (2)	 **13b**; 86; (8)

^{a} Yield based on the isolated product. ^{b} Yield of the reaction with diacetoxydimethylsilane.

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to the reactions of the corresponding dihydroperoxyperoxides with dichlorodimethylsilane **7a**. Peroxides **8**−**13** are stable on storage at 0 °C and can be purified by silica gel chromatography and recrystallized from anhydrous solvents. Some of these compounds have very high melting points, which are not typical of peroxides; for example, the melting points of **12a** and **13a** are 264−266 and 156−158 °C, respectively. At these temperatures, peroxides ROOR (R = alkyl) generally undergo decomposition accompanied by the O−O bond cleavage. A comparison of thermal stability of 1,2,4,5,7,8-hexaoxa-3-silonanes **8a**, **9a**,

TABLE 3. Hydrolysis of 1,2,4,5,7,8-Hexaoxa-3-silonanes[a]

run	1,2,4,5,7,8-hexa-oxa-3-silonane	time of complete hydrolysis of 1,2,4,5,7,8-hexa-oxa-3-silonanes, h	yield of dihydro-peroxyperoxides **1**, **2**, and **5**,[b] %
1	**8a**	0.1	84
2	**8b**	2.5	85
3	**9a**	0.17	91
4	**9b**	3.7	86
5	**12a**	1.5	93 (9)[c]
6	**12b**	23	94

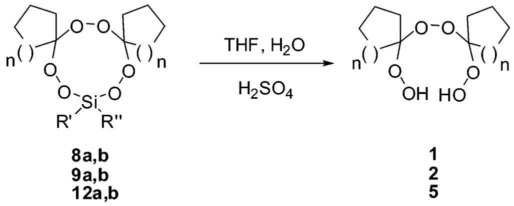
[a] General reaction conditions for the hydrolysis: hexaoxasilonane (0.31 mmol) was dissolved in a solution (10 g) containing THF (9.78 g), H_2O (0.2 g), and H_2SO_4 (0.02 g), and the reaction mixture was kept at 6 °C until the complete conversion of hexaoxasilonane was achieved (TLC monitoring). [b] Yield based on the isolated product. [c] The hydrolysis time was 0.1 h.

and **12a** with nonsilylated analogs—1,2,4,5,7,8-hexaoxonanes[16]—shows that these peroxides behave similarly: they could be stored without a noticeable decomposition for 2−3 months at temperatures below 0 °C, at room temperature the decomposition of **8a** and **9a** occurs noticeably for 1 month. The structures of the resulting compounds were established by NMR spectroscopy and elemental analysis. Since 1,2,4,5,7,8-hexaoxa-3-silonanes have been previously unknown, it was important to obtain direct evidence for the existence of these compounds by X-ray diffraction. The X-ray diffraction study was carried out for compounds **12a**,**b** (Figure 1, X-ray data are included in the Supporting Information).

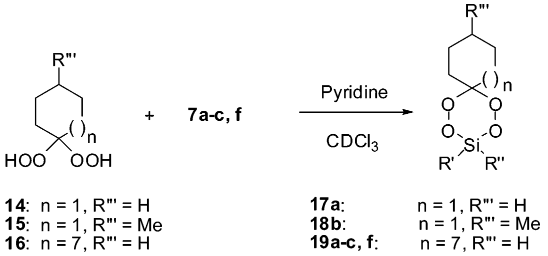
In both molecules, the nine-membered rings adopt a twist-boat-chair conformation (pseudo-C_3 conformer); the average Si−O, O−O, and C−O bond lengths are 1.666(4), 1.474(5), and 1.419(6) Å, respectively. The crystal structures are typical of branched hydrocarbons, with hydrophobic space-filling contacts reflecting the simple close-packing of hydrophobic molecules.[17]

Hydrolysis of Hexaoxasilonanes in an Acidic Medium. The resulting 1,2,4,5,7,8-hexaoxa-3-silonanes are unstable in the presence of acids and are decomposed by water. The hydrolysis of hexaoxasilonanes was found to result in the virtually complete transformation of these compounds into 1,1′-dihydroperoxyperoxides (84−94% yields). Hence, the dialkylsilyl fragment can be considered as a convenient protecting group for 1,1′-dihydroperoxyperoxides. According to the results of the hydrolysis of hexaoxasilonanes **8a**,**b**, **9a**,**b**, and **12a**,**b** in THF containing 2% of water and 0.2% of sulfuric acid, the stability of these compounds increases with increasing size of the alicycle and the volume of the substituents at the silicon atom (Scheme 2, Table 3).

SCHEME 2. Hydrolysis of 1,2,4,5,7,8-Hexaoxa-3-silonanes



SCHEME 3. Synthesis of 1,2,4,5-Tetraoxa-3-silinanes



The differences in the hydrolysis rate of 1,2,4,5,7,8-hexaoxa-3-silonanes in going from dimethylsilyl to diethylsilyl derivatives are substantial, and the hydrolysis time increases by a factor of ca. 15−25. An increase in the size of the alicycle has a smaller effect on the hydrolytic stability of 1,2,4,5,7,8-hexaoxa-3-silonanes.

Synthesis of 1,2,4,5,3-Tetraoxa-3-silinanes. Based on the knowledge of the ring strain, 1,2,4,5-tetraoxa-3-silinanes would be expected to be produced selectively to form stable six-membered rings. However, our expectations were not completely fulfilled. The results of the reactions of dialkyldichlorosilanes **7a**−**c**,**f** with 1,1-bishydroperoxides **14**−**16** (Scheme 3) differ substantially from those with dihydroperoxyperoxides **1**−**5** (Scheme 1).

Under the conditions analogous to the synthesis of **8**−**13**, 1,2,4,5-tetraoxa-3-silinanes **17**−**19** were isolated in the individual state in none of the experiments. These compounds did not withstand the purification on different (including silanized) SiO_2 and Al_2O_3. Attempts to separate tetraoxasilinanes from amines led to the formation of silicon-containing oligomers. The NMR monitoring of the reaction proceeding according to

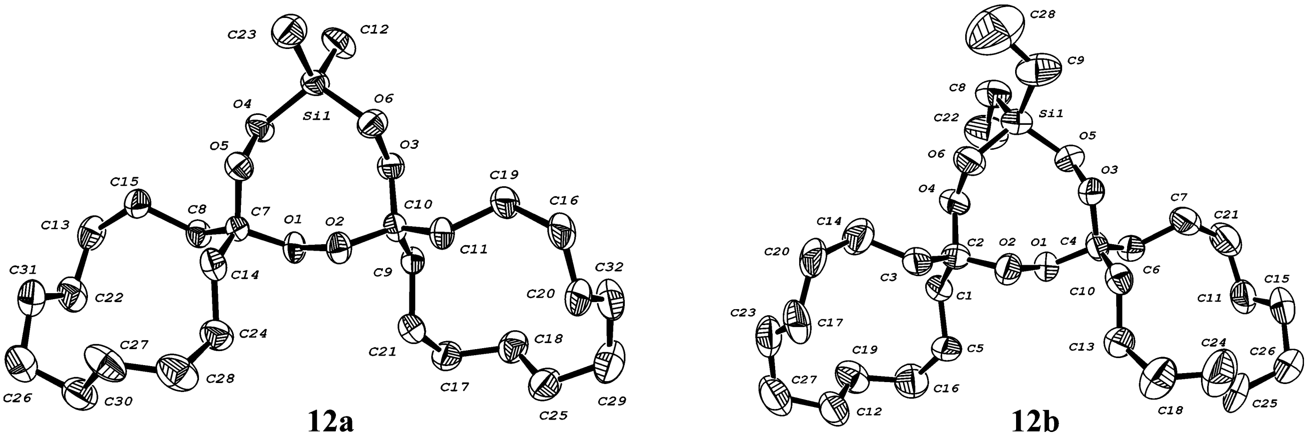


FIGURE 1. Molecular structure of **12a**,**b**, showing the atomic numbering and 40% probability displacement ellipsoids. H atoms omitted for clarity.

Scheme 3 in $CDCl_3$ in the presence of pyridine showed that 1,2,4,5-tetraoxa-3-silinanes **17**−**19** are formed as virtually the only products, but they undergo decomposition (10−20 h). Apparently, these compounds are stable over a period of time in dilute solutions in the presence of amines, with which these compounds form rather stable complexes.

Conclusion

A general procedure was developed for the synthesis of 1,2,4,5,7,8-hexaoxa-3-silonanes, new class of cyclic peroxides, containing one Si atom and three O−O fragments in one ring. The method is based on the reaction of 1,1′-dihydroperoxyperoxides with disubstituted dialkylsilanes in the presence of aromatic nitrogen bases. The main reaction pathway involves the formation of cyclic rather than oligomeric (linear) peroxides. In contradiction to the common rule of the steric strain of the carbocyclic structures, the nine-membered cyclic peroxides 1,2,4,5,7,8-hexaoxa-3-silonanes are much more stable than their six-membered cyclic analogs 1,2,4,5-tetraoxa-3-silinanes, which were isolated in the individual state in none of the experiments. The formation of 1,2,4,5-tetraoxa-3-silinanes was detected by NMR spectroscopy in the reaction of dialkyldichlorosilanes with *gem*-bishydroperoxides.

Experimental

Caution: Although we have encountered no difficulties in working with peroxides, precautions, such as the use of shields, fume hoods, and the avoidance of transition-metal salts, heating, and shaking, should be taken whenever possible. It should be mentioned that although some 1,2,4,5,7,8-hexaoxonanes display remarkable sensitivity towards friction or shock,[17,18] similar 1,2,4,5,7,8-hexaoxa-3-silonanes are more stable under these conditions.

Synthesis of 17,17-Diethyl-7,8,15,16,18,19-hexaoxa-17-siladispiro[5.2.5.5]nonadecane, 9b. 1,1′-Dihydroperoxydi(cyclohexyl)peroxide **2** (0.15 g, 0.57 mmol) was added to a solution of imidazole (0.12 g, 1.76 mmol) and dichlorodiethylsilane **7b** (0.11 g, 0.70 mmol) in THF (6 mL). The reaction mixture was stirred at 20−25 °C for 3 h and then filtered. The residue was washed with THF (2 × 5 mL). The filtrate was concentrated, and **9b** was isolated by flash chromatography using a short silica gel column (hexane−CH_2Cl_2, 20:1): yield 84% (0.166 g, 0.48 mmol); white crystals; mp = 44−45 °C; R_f 0.52 (TLC, hexane−EA, 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (q, 4H, J = 7.5 Hz), 1.04 (t, 6H, J = 7.5 Hz), 1.34−1.99 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.4, 6.4, 22.7, 25.6, 30.1, 30.2, 108.5. Anal. Calcd for $C_{16}H_{30}O_6Si$: C, 55.46; H, 8.73; Si, 8.11. Found: C, 55.64; H, 8.63; Si, 8.37.

Synthesis of Ethyl 4-(29-Methyl-13,14,27,28,30,31-hexaoxa-29-siladispiro[11.2.11.5]hentriacont-29-yl)butanoate, 12g. 1,1′-Dihydroperoxydi(cyclododecyl)peroxide **5** (0.2 g, 0.47 mmol) was added to a solution of imidazole (0.095 g, 1.40 mmol) and ethyl 4-[dichloro(methyl)silyl]butanoate **7g** (0.13 g, 0.57 mmol) in THF (8 mL). The reaction mixture was stirred at 20−25 °C for 12 h and then filtered. The residue was washed with THF (2 × 5 mL). The majority (∼15 mL) of the filtrate was evaporated, and MeOH (15 mL) was added. The residue of **12g** was precipitated. The suspension was cooled at −10 °C, and the residue of **12g** was filtered. Peroxide **12g** was washed with MeOH (4 × 5 mL) and dried under reduced pressure (10−20 Torr) at room temperature for 2 h: yield 74% (0.203 g, 0.35 mmol); white crystals; mp = 97−99 °C; R_f 0.36 (TLC, hexane−EA, 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 3H), 0.83 (t, 2H, J = 6 Hz) 1.18−1.89 (m, 49H), 2.38 (t, 2H, J = 7.3 Hz), 4.15 (q, 2H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −6.6, 11.7, 14.3, 18.6, 19.2, 19.5, 21.9, 22.2, 25.9, 26.2, 26.4, 37.1, 60.1, 112.6, 173.5. Anal. Calcd for $C_{31}H_{58}O_8Si$: C, 63.44; H, 9.96; Si, 4.79. Found: C, 63.38; H, 9.62; Si, 4.80.

Hydrolysis of 15,15-Diethyl-6,7,13,14,16,17-hexaoxa-15-siladispiro[4.2.4.5]heptadecane, 8b. Peroxide **8b** (0.1 g, 0.31 mmol) was added to a solution of THF (9.78 g), H_2O (0.2 g), and H_2SO_4 (0.02 g) at 6 °C. The mixture was kept at this temperature for 2.5 h (TLC monitoring) for a complete hydrolysis of **8b**. K_2CO_3 (0.5 g) was added to the mixture, and the suspension was stirred at room temperature for 0.5 h. The suspension was filtered, and the filtrate was concentrated. 1,1′-Dihydroperoxydi(cyclopentyl)peroxide **1** was isolated by silica gel column chromatography (hexane−Et_2O, 10:1): yield 85% (0.063 g, 0.27 mmol); white crystals; mp = 60−63 °C; ^{1}H NMR (200.13 MHz) δ 1.55−1.82 (m, 8H), 1.83−2.11 (m, 8H), 9.80−10.05 (br s, 2H); ^{13}C NMR (50.32 MHz) δ 24.4, 33.2, 122.2.

Acknowledgment. This work is supported by the Program for Support of Leading Scientific Schools of the Russian Federation (Grant No. NSh 5022.2006.3), the Grant of President of Russian Federation (No. MK-3515.2007.3), and the Russian Science Support Foundation.

Supporting Information Available: Experimental procedures for the synthesis of 1,2,4,5,7,8,3-hexaoxasilonanes **8**−**13**, 1,2,4,5,3-tetraoxasilinanes **17**−**19**, 1,1′-dihydroperoxyperoxides **1**−**6**, and *gem*-bishydroperoxides **14**−**16**, ^{1}H and ^{13}C NMR spectra for all peroxides, and details of X-ray data for **12a** and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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