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# Organosilicon and organogermanium peroxides: synthesis and reactions

A O Terent'ev, M M Platonov, D O Levitsky, V M Dembitsky

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**Abstract. The methods of synthesis and reactions of organosilicon and organogermanium peroxides are surveyed. The emphasis is placed on the studies reported in the last two decades, because in this period, the use of singlet oxygen and the Isayama – Mukaiyama reaction for the synthesis of organosilicon peroxides started. The use of these compounds in the development of antiparasitic agents is considered. The bibliography includes 220 references.**

## I. Introduction

Pioneering studies [1 – 3] on chemistry of organosilicon and organogermanium peroxides were reported in the late 1950s. Since then, a number of reviews on the subject appeared. Among them, noteworthy are the works by Sosnovsky and Brown (1966),[4] Brandes and Blaschette (1974),[5, 6] Alexandrov (1979, 1982 and 1989),[7 – 10] Yablokov (1980),[11] Kucher (1981),[12] Voronkov (1991),[13] Ricci (1996),[14] Tamao (2002),[15] Ando (2006) [16] and Davies (2007).[17] However, the most recent reviews are mainly focused on physical chemistry of the title compounds.

Organic peroxides are a rather widespread and needed class of compounds.[18 – 24] They are widely used in industrial and laboratory synthesis as oxidants, polymerization initiators, cross-linking agents, 'building blocks' and intermediate products. Some of them also exhibit antimalarial, antimicrobial and antitumour activities.

Peroxides containing the Si—O—O unit have similar fields of application. They are mainly used for the synthesis of high-molecular-mass compounds,[1, 25 – 32] as well as hydroxylating,[33 – 35] peroxidizing [36 – 42] and oxidizing agents.[43 – 45] Silicon peroxides are formed as intermediates in the Fleming and Tamao – Kumada oxidation reactions.[46 – 52] However, the chemistry of organosilicon peroxides is poorly developed due to a limited number of methods of their synthesis. There are several general approaches to the synthesis of peroxides containing the Si—O—O unit. They are based on the reactions of chlorosilanes with hydroperoxides in the presence of bases,[53 – 61] of the system $CoL_2 - O_2 - Et_3SiH$ (L is a ligand) with unsaturated compounds (the Isayama – Mukaiyama reaction) [62 – 66] and of singlet oxygen with enol silyl ethers.[67 – 73] At present, these methods are used to obtain mainly linear mono-, di-, tri- and tetraperoxy-substituted silanes. There are also about twenty known structures in which the Si—O—O unit is part of a ring.[74 – 81]

Organogermanium peroxides belong to a poorly studied class of compounds including about thirty substances known to date.[3, 82, 83] They are usually synthesized by condensation of hydroperoxides with halogermanes,[3, 82, 83] triphenylethoxygermane and triphenylaminogermane.[82]

The advances in the chemistry of organosilicon and organogermanium peroxides are inseparably linked with the results of earlier investigations. Because of this, key studies on the subject reported since 1956 are quoted in the present review. Emphasis is placed on the results obtained in the studies carried out during the last two decades. In this period, the use of singlet oxygen and the Isayama – Mukaiyama reaction for the synthesis of organosilicon peroxides gave a new impetus to the development of this branch of chemistry. In addition, silicon peroxides are

**A O Terent'ev, M M Platonov** N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119991 Moscow, Russian Federation. Fax (7-499) 135 53 28, e-mail: terentev@ioc.ac.ru (A O Terent'ev), plmm@bk.ru (M M Platonov)
**D O Levitsky** University of Nantes, Faculty of Sciences and Technology, rue de la Houssinière 2, BP 92208 44322 Nantes, Cedex3, France. Fax (33-251) 811 578, e-mail: Dmitri.Levitsky@univ-nantes.fr
**V M Dembitsky** Hebrew University of Jerusalem, Faculty of Medicine, Institute for Drug Research, P.O. Box 12065, 91120 Jerusalem, Israel, e-mail: dvalery@cc.huji.ac.il

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actively used as intermediates in the synthesis of substances with antiparasitic activity. Unlike the previous papers, this review presents to the fullest extent the organic chemistry of silicon and germanium peroxides.

$$R^1_3E—O—O—R^2$$

E = Si, Ge; $R^1$ = Alk, OAlk, *etc.*; $R^2$ = H, $CAlk_3$, $SiAlk_3$, $GeAlk_3$, *etc.*

Modern methods of their synthesis and known reactions are considered.

## II. The synthesis of organosilicon peroxides using hydroperoxides or their salts

Most organosilicon peroxides were obtained by the reaction of nucleophilic substitution at the silicon atom involving replacement of the leaving group by the peroxide one.

Reactions of hydroperoxides with chlorosilanes in the presence of bases represent the most convenient method of synthesis of peroxysilanes. The advantages of this method include the availability of the parent substances and simple experimental design. Mono-, di, tri- and tetrachlorosilanes ($n = 1-4$) easily enter the reaction that results in the corresponding peroxysilanes.[54]

$$n\,R^1OOH + R^2_{4-n}SiCl_n \longrightarrow R^2_{4-n}Si(OOR^1)_n + n\,HCl.$$

Bases with a donor nitrogen atom, such as ammonia,[56,84,85] pyridine,[1,53–55,86] imidazole[81,87] and triethylamine[88] are used as HCl acceptors. In some cases, when the reaction is carried out without bases, the yield of the desired product significantly decreases.[53] Usually, low-boiling hydrocarbons (petroleum ether, pentane and hexane)[53,55] or diethyl ether[1,85,88] are used as solvents. The temperature range varies from $-15$ °C[1] to 25 °C.[85]

Reactions of hydroxyperoxides **1** with monochlorosilanes **2** in the presence of the bases listed above usually lead to good yields of the corresponding monoperoxides **3** [see Eqn (1)]. This is a general reaction. The structures of the parent compounds have little effect on the yields of organosilicon peroxides (Table 1).

$$\underset{\mathbf{1}}{R^1OOH} + \underset{\mathbf{2}}{R^2R^3R^4SiCl} \longrightarrow \underset{\mathbf{3}}{R^2R^3R^4SiOOR^1} + HCl. \qquad (1)$$

Reactions of monochlorosilanes **2** with hydrogen peroxide result in products **4** or **5** depending on the reactant ratio.

$$\underset{\mathbf{2a-c}}{H_2O_2} + R^1R^2_2SiCl \longrightarrow \underset{\mathbf{4a-c}}{R^1R^2_2SiOOH} + HCl,$$

$R^1 = R^2$ = Me (**a**),[1] Ph (**b**);[59] $R^1$ = 4-$MeC_6H_4$, $R^2$ = Ph (**c**, 63%).[91]

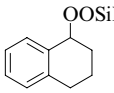
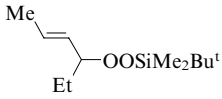
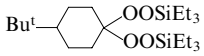
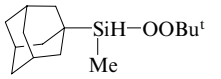
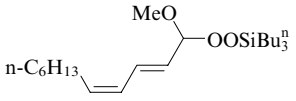
$$\underset{\mathbf{2a,c-e}}{H_2O_2} + 2\,R^1R^2_2SiCl \longrightarrow \underset{\mathbf{5a,c-e}}{R^1R^2_2SiOOSiR^1R^2_2} + 2\,HCl,$$

$R^1 = R^2$ = Me (**a**, 43%),[1] Et (**d**);[85]

$R^1$ = 4-$MeC_6H_4$: $R^2$ = Ph (**c**, 72%),[91] Me (**e**, 30%).[92]

Hydroperoxysilanes **4** are unstable substances. Hydroperoxytriphenylsilane **4b** is most stable among the compounds $R_3SiOOH$. It is used for the synthesis of asymmetric peroxysilanes **6**.

**Table 1**. Synthesis of monoperoxysilanes **3** using reaction (1).

| Compound | Yield (%) | Ref. |
|---|---|---|
| $Me_3SiOOBu^t$ | 54 | 1 |
| | 89 | 53 |
| $Me_3SiOOCMe_2Ph$ | 49 | 53 |
| $Me_3SiOOCMe_2Et$ | 83 | 53 |
|  | 98 | 53 |
| $(Pr^nO)Me_2SiOOBu^t$ | 70 | 54 |
| $(Bu^tO)Me_2SiOOBu^t$ | 60 | 54 |
| $(CH_2{=}CH)MeEtSiOOBu^t$ | 59 | 55 |
| $(MeO)Me_2SiOOBu^t$ | 40 | 56 |
| $(EtO)Me_2SiOOBu^t$ | 76 | 56 |
| $(MeO)_2MeSiOOBu^t$ | 80 | 56 |
| $(MeO)_2MeSiOOCMe_2Et$ | 71 | 56 |
| $(EtO)_2MeSiOOBu^t$ | 60 | 56 |
| $(Me_3SiOOCMe_2CH_2)_2$ | 81 | 56 |
|  | 48 | 87 |
|  | 75 | 88 |
| $Ph(CH_2)_2CMe(OOSiEt_3)_2$ | 49 | 88 |
|  | 84 | 89 |
|  | 42 | 90 |

$$\underset{\mathbf{4b}}{Ph_3SiOOH} \xrightarrow[(\mathbf{2})]{R^1R^2_2SiCl} \underset{\mathbf{6}}{Ph_3SiOOSiR^1R^2_2}$$

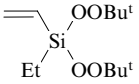
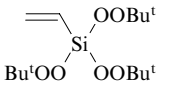
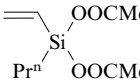
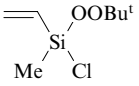
| $R^1$ | $R^2$ | Yield (%) | Ref. |
|---|---|---|---|
| Me | Me | 70 | 93 |
| Ph | Me | – | 94 |
| Et | Et | 50 | 59 |
| $Pr^n$ | $Pr^n$ | 50 | 59 |
| $Bu^n$ | Me | 35 | 58 |
| $Bu^n$ | $Bu^n$ | 50 | 59 |
| 4-$BrC_6H_4$ | Me | 30 | 58 |
| 4-$MeC_6H_4$ | Me | 50 | 58 |
| 4-$MeOC_6H_4$ | Me | 20 | 58 |

The structures of the products of the reactions of alkyl hydroperoxides with di-, tri- and tetrachlorosilanes depend on the molar ratio of the parent compounds. When the hydroperoxide is taken in excess, peroxysilanes are formed. Reactions of chlorosilanes with hydroperoxides at reactant ratios of 1 : (< 1) afford peroxychlorosilanes (Table 2).

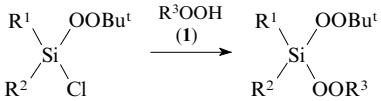
Peroxychlorosilanes **7** are the starting compounds in the synthesis of organosilicon diperoxides **8** containing different alkylperoxy groups at the silicon atom.[96,97]

In the presence of bases, peroxychlorosilanes **7** react with alcohols,[98,99] amines[98] and carboxylic acids[100] result-

**Table 2**. Examples of polyperoxysilanes and peroxychlorosilanes.

| Compound | Yield (%) | Ref. |
|---|---|---|
| $MeSi(OOBu^t)_3$ | 56 | 53 |
| $Et_2Si(OOBu^t)_2$ | 60 | 53 |
| $Si(OOBu^t)_4$ | 90 | 53 |
| $Me_2Si(OOBu^t)_2$ | 51 | 54 |
| $ClMe_2SiOOBu^t$ | 43 | 54 |
| $Cl_3SiOOBu^t$ | 31 | 54 |
|  | 60 | 55 |
|  | 40 | 55 |
| $(MeO)MeSi(OOBu^t)_2$ | 68 | 56 |
| $(EtO)MeSi(OOBu^t)_2$ | 55 | 56 |
|  | 66 | 86 |
| $ClMe_2SiOOBu^t$ | 56 | 95 |
|  | 58 | 95 |

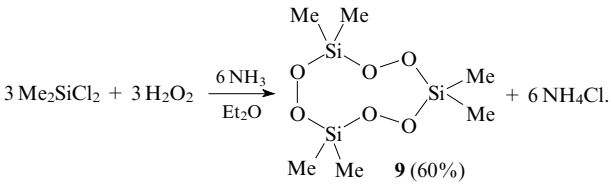
ing in the corresponding Si-functionalized organic peroxides.



**7** **8**

| $R^1$ | $R^2$ | $R^3$ | Yield (%) | Ref. |
|---|---|---|---|---|
| Me | Me | $Bu^s$ | 80 | 96, 97 |
| Me | Me | $Me_2EtC$ | 89 | 96, 97 |
| Me | Me | $Me_2(cyclo\text{-}C_6H_{11})C$ | 80 | 96 |
| Et | Et | $Me_2EtC$ | 88 | 96, 97 |
| Me | Ph | $Me_2EtC$ | 92 | 96, 97 |

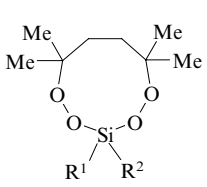
The nine-membered cyclic peroxide **9** containing three silicon atoms and three peroxide groups in the ring was obtained by the reaction of hydrogen peroxide with dimethylchlorosilane in diethyl ether in the presence of ammonia.[79]



**9** (60%)

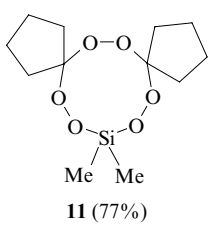
The structure of peroxide **9** was studied by X-ray diffraction analysis. The average value of the torsion angle Si–O–O–Si is 135.6° and the peroxide bridges have a nearly *trans*-conformation. The average Si–O bond length equal to 1.674 Å is longer than that in siloxanes (< 1.64 Å). The average O–O distance (1.492 Å) noticeably exceeds the corresponding distance in acyclic organic peroxides, being slightly longer than the O–O distances in the cyclic carbon analogue, acetone triperoxide (1.472–1.483 Å), and in trimethyl(trimethylsilylperoxy)silane (1.481 Å).

Organosilicon diperoxide rings (1,2,4,5-tetraoxa-3-silonanes) **10a–e**[80] and triperoxide rings (1,2,4,5,7,8-hexaoxa-3-silonanes) **11–14**[81] were obtained using dichlorosilanes.

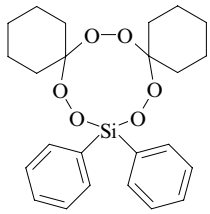


**10a–e**

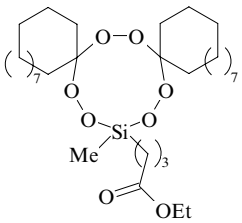
$R^1 = R^2 = Me$ (**a**, 62%), Et (**b**), $R^1 = Me$: $R^2 = Ph$ (**c**), $CH_2{=}CH$ (**d**), $n\text{-}C_5H_{11}$ (**e**).



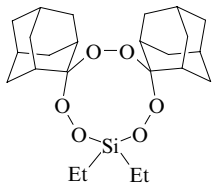
**11** (77%)



**12** (79%)

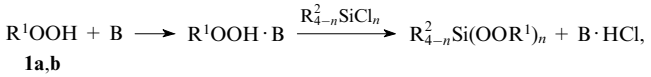


**13** (81%)



**14** (86%)

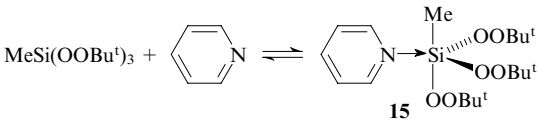
Amines have various functions in nucleophilic substitution reactions at silicon. First, they act as HCl acceptors. Second, they increase the nucleophilicity of the reacting hydroperoxides[61] and in some cases form stable adducts with hydroperoxides.[60] These adducts can be isolated and used for the peroxidation of silanes. Thirty-five peroxysilanes were synthesized using the method based on the formation of stable adducts of *tert*-butyl hydroperoxide (**1a**) and cumyl hydroperoxide (**1b**) with amines. The yields varied from 55% to 95%. 1,4-Diazabicyclo[2.2.2]octane (DABCO) and urotropine (HEXA) were used as complex-forming agents. The formulae and yields of some compounds are listed below.



**1a**,**b**

B = DABCO, HEXA;
for $R^1 = Bu^t$ (**1a**) $n = 1$: $R^2_3 = Me_3$ (91%), $Bu^n_3$ (95%);
$n = 2$: $R^2_2 = Me_2$ (76%), $(CH_2{=}CH)Me$ (92%), $(CH_2{=}CH)Ph$ (95%);
$n = 3$: $R^2 = H$ (55%), All (80%); $n = 4$ (64%);
for $R^1 = CMe_2Ph$ (**1b**) $n = 1$: $R^2_3 = Me_3$ (75%), $Bu^n_3$ (95%), $(CH_2{=}CH)Ph_2$ (92%), $(ClCH_2)Me_2$ (95%);
$n = 2$, $R^2_2 = Me_2$ (85%);
$n = 3$: $R^2 = n\text{-}C_6H_{13}$ (95%), Ph (61%); $n = 4$ (64%).

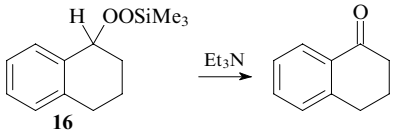
Nucleophilic substitution reactions can be accompanied by complexation of tertiary amines with the starting silanes[101] and with the silyl peroxides obtained.[102, 103] This was proved by $^1H$ NMR spectroscopy[102] and calorimetry.[103] Presumably, the reaction of pyridine with tris(*tert*-butylperoxy)methylsilane results in the donor–acceptor complex **15**.[104]




**15**

The formation of such a complex leads to an increase in the decomposition rate of the peroxide.[104]

The base used in the nucleophilic substitution reactions at the silicon atom may catalyze the decomposition of peroxysilanes, *e.g.*, compound **16**.[53]



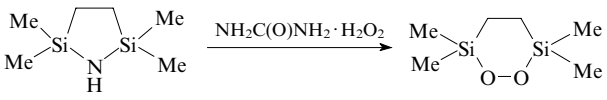

**16**

Monoperoxysilanes **3** are also obtained by the reaction of silylamines **17** with hydroperoxides **1**. The reaction is carried out in the temperature range from 0 °C [61] to 20 °C.[77] In some cases, it is conducted at a reduced pressure to remove the amine formed from the reaction sphere.[105] This method was used to synthesize not only simple monoperoxysilanes **3**, but also their more complicated analogues **18** [77] and **19** (from compounds **20** and **21**, respectively).[106]

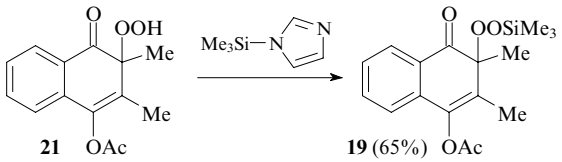
$$R^1R^2_2SiNR^3_2 + R^4OOH \longrightarrow R^1R^2_2SiOOR^4 + NHR^3_2$$

**17** **3**

| $R^1$ | $R^2$ | $NR^3_2$ | $R^4$ | Yield (%) | Ref. |
|---|---|---|---|---|---|
| Me | Me | NHAlk | Bu$^t$ | 20 | 107 |
| Me | Me | $NH_2$ | $Ph_3Ge$ | 75 | 93 |
| Et | Et | $NEt_2$ | Bu$^t$ | 52 | 105 |
| n-$C_6H_{13}$ | n-$C_6H_{13}$ | $NH_2$ | H | 83 | 61 |
| Bn | Bn | $NH_2$ | H | 63 | 61 |
| Ph | Ph | $NH_2$ | $Ph_3Ge$ | 85 | 93 |
| Ph | Ph | $NH_2$ | H | 55 | 61 |
| Ph | Me | $NH_2$ | H | 54 | 61 |




**20** **18** (68%)




**21** **19** (65%)

High yields of peroxysilanes **3** were also obtained by the reaction of chlorosilanes **2** with the hydroperoxide salts **22** (M = Li, Na, MgCl).[107–109] The process is carried out in hexane or ether at room temperature and the reaction takes from 1 to 3 h to complete.

$$R^1_3SiCl + R^2OOM \longrightarrow R^1_3SiOOR^2 + MCl$$

**2** **22** **3**

| $R^1$ | $R^2$ | M | Yield (%) | Ref. |
|---|---|---|---|---|
| Me | Bu$^t$ | Li | 70 | 108 |
| Me | Bu$^t$ | Na | 80 | 109 |
| Ph | $Ph_3C$ | Na | 96 | 109 |

A similar reaction using $Na_2O_2$ and two equivalents of trimethylchlorosilane results in $Me_3SiOOSiMe_3$ (**5a**).[107]

Reactions of dialkyl(aryl)dichlorosilanes with alkylperoxymagnesium chloride taken in a 1 : 1 ratio afford disubstituted (alkylperoxy)chlorosilanes **7** in moderate yields.[96]

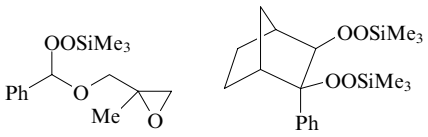
$$R^1R^2SiCl_2 + Bu^tOOMgCl \longrightarrow R^1R^2Si(OOBu^t)Cl + MgCl_2$$

**7**

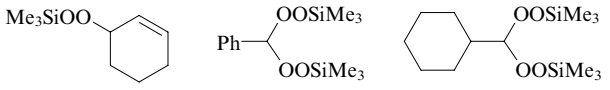
| $R^1$ | $R^2$ | Yield (%) |
|---|---|---|
| Me | Me | 45 |
| Et | Et | 23 |
| $CH_2$=CH | Me | 60 |
| $ClCH_2$ | Me | 54 |
| Ph | Me | 45 |

The substitution of the second chlorine atom occurs with difficulty. Peroxides with the general formula $R^1R^2Si(OOBu^t)_2$ are formed in small amounts (about 6%) even if alkylperoxymagnesium chloride is taken in a large excess. The remaining chlorine atom can be replaced only upon treatment of diorgano(*tert*-butylperoxy)chlorosilane with the corresponding hydroperoxide in the presence of a base.[96]

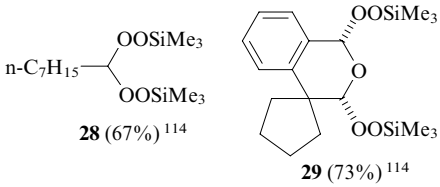
A method of synthesis of trimethylsilyl peroxides based on the reaction of hydroperoxides with *N*,*O*-bis(trimethylsilyl)acetamide (BSA) was used to obtain mono- and bis(silyl)peroxides **23**–**29**.[110–114]




**23** (see [110]) **24** (56%) [111, 112]



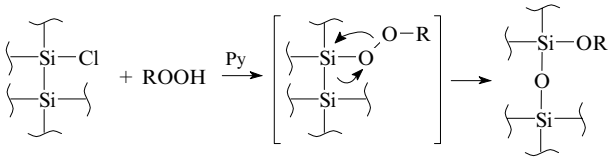

**25** (Ref. 113) **26** (66%) [114] **27** (50%) [114]




**28** (67%) [114] **29** (73%) [114]

Unlike chlorosilanes, chlorodisilanes react with hydroperoxides or their lithium salts with the formation of alkoxydisiloxanes (R = Alk) and peroxydisiloxanes which are the products of oxidation of the Si–Si bond (Scheme 1).[115, 116]

Scheme 1




Alkoxydisiloxanes and peroxydisiloxanes may be obtained both by replacement of the chlorine atom by an organoperoxy group followed by rearrangement of the

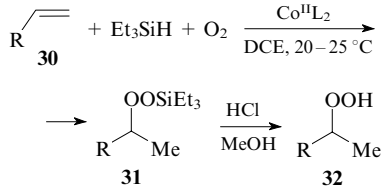
disilanyl peroxide (see Scheme 1) and as a result of oxidation of the Si—Si bond followed by the formation of chlorodisiloxane and alcohol (or alcoholate in the case of a lithium salt of a peroxide[108, 116–119]) and subsequent replacement of the chlorine atom in the chlorodisiloxane by an alkoxyl or peroxyl radical.

$$R_3Si—SiR_2Cl + Bu^tOOLi \longrightarrow R_3Si—O—SiR_2Cl + Bu^tOLi \longrightarrow$$
$$\longrightarrow R_3Si—O—SiR_2OBu^t,$$
$$R_3Si—O—SiR_2Cl + Bu^tOOLi \longrightarrow R_3Si—O—SiR_2OOBu^t.$$

## III. Synthesis of organosilicon peroxides using the Isayama–Mukaiyama reaction

The Isayama–Mukaiyama reaction is a convenient method of synthesis of peroxysilanes from alkenes. Pioneering studies[63, 64] concerning this process date back to 1989. Since then, this reaction has played a significant role in the synthesis of peroxides. About twenty papers dealing with the synthesis of complex peroxide molecules using this reaction as a key step of the synthesis were reported during two decades since its discovery.[40, 41, 42, 66, 120–131]

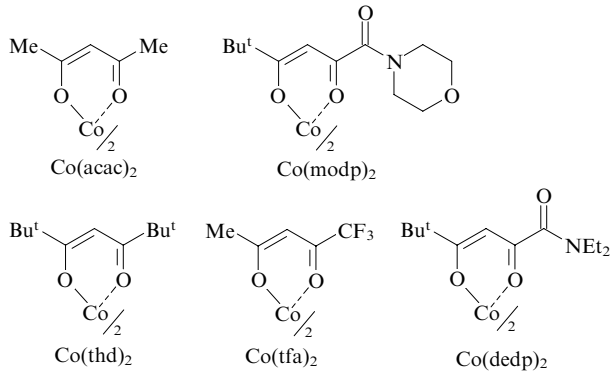
The Isayama–Mukaiyama reaction is based on the oxidation of alkenes **30** by molecular oxygen catalyzed by bis(1,3-diketonato) cobalt(II) in the presence of triethylsilane. It allows one to synthesize the triethylsilyl peroxides **31** selectively and in high yield. Subsequent treatment of these compounds with methanol in the presence of catalytic amounts of HCl leads to desilylation and the formation of hydroperoxides **32**.



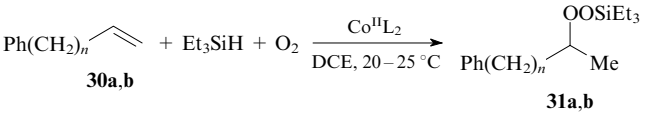

(2)

DCE is 1,2-dichloroethane.

Reaction (2) can be catalyzed by bis(1,3-diketonato)-cobalt(II): bis(acetylacetonate)[Co(acac)$_2$], bis(1,1,1-trifluoropentan-2,4-dionate)[Co(tfa)$_2$], bis[1-(*N*-diethylcarbamoyl)-4,4-dimethylpentan-1,3-dionate][Co(dedp)$_2$], bis[1-(morpholin-4-ylcarbonyl)-4,4-dimethylpentan-1,3-dionate][Co(modp)$_2$] and bis(2,2,6,6-tetramethylheptane-3,5-dionate)[Co(thd)$_2$].




The structure of the ligand in bis(1,3-diketonato)cobalt(II) significantly affects the yield of the target products. For example, peroxysilylation of styrene (**30a**)[63] in the presence of Co(modp)$_2$ results in triethylsilyl peroxide **31a** in a yield of 96%. However, the use of Co(acac)$_2$ as catalyst causes the product yield to decrease to 30% (Table 3).




$n$ = 0 (**a**), 2 (**b**).

In the case of peroxysilylation of 4-phenylbut-1-ene (**30b**), the highest yield of 1-phenyl-3-(triethylsilylperoxy)-butane (**31b**) was obtained with Co(acac)$_2$ as catalyst (see Table 3).[62]

**Table 3**. Peroxysilylation of alkenes in the presence of bis(1,3-diketonato)cobalt(II).

| Compound | L | Reaction time /h | Alkene conversion (%) | Yield of silyl peroxide (%) | Ref. |
|---|---|---|---|---|---|
| **30a** | acac | 24 | 52 | 30 | 63 |
| | tfa | 12 | 82 | 73 | 63 |
| | dedp | 3 | 100 | 94 | 63 |
| | modp | 3 | 100 | 96 | 63 |
| **30b** | acac | 5 | 100 | 94 | 62 |
| | thd | 5 | 100 | 90 | 62 |
| | tfa | 12 | 90 | 80 | 62 |
| | modp | 3 | 100 | 92 | 62 |

**Note**. Reaction conditions: alkene (1 mmol) and triethylsilane (2 mmol) are stirred in dichloroethane (5 ml) in the presence of bis(1,3-diketonato)cobalt(II) (0.05 mmol) in oxygen atmosphere at room temperature.

The nature of the solvent in which the Isayama–Mukaiyama reaction is carried out influences significantly the yield of the target product.[63] Under similar conditions, the highest yields of 1-phenyl-3-(triethylsilylperoxy)butane (**31b**), namely, 94% and 92%, were obtained in dichloroethane and benzene, respectively (*cf.* 75% in ethyl acetate). No conversion of the initial 4-phenylbut-1-ene[34] was observed at all in n-propyl alcohol at room temperature (Table 4).

**Table 4**. Effect of the solvent nature on the yield of 1-phenyl-3-(triethylsilylperoxy)butane (**31b**).

| Solvent | Reaction time /h | Alkene conversion (%) | Yield of silyl peroxide (%) |
|---|---|---|---|
| Dichloroethane | 5 | 100 | 94 |
| Benzene | 12 | 100 | 92 |
| Ethyl acetate | 24 | 82 | 75 |
| n-Propyl alcohol | 24 | 0 | 0 |

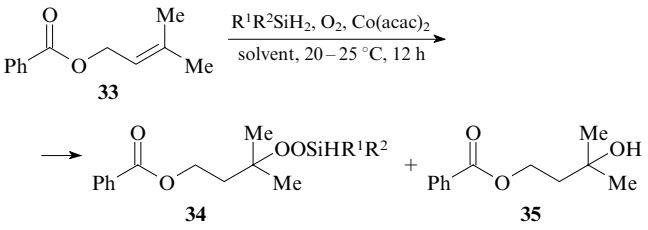
The Isayama–Mukaiyama reaction carried out using dialkylsilanes instead of triethylsilane in the presence of 3-methylbut-2-enyl benzoate (**33**) leads to the formation of the corresponding peroxysilane **34** and a side product, 3-hydroxy-3-methyl benzoate (**35**).[64] The reaction in the

**Table 5**. Reactions of 3-methylbut-2-enyl benzoate (**33**) with $O_2$ and substituted silanes in the presence of $Co(acac)_2$.

| Silane | Solvent | Alkene conversion (%) | Yield (%) | |
|---|---|---|---|---|
| | | | **34** | **35** |
| $Et_2SiH_2$ | Dichloroethane | 100 | 90 | 5 |
| $Ph_2SiH_2$ | Dichloroethane | 85 | 60 | 20 |
| $PhSiH_3$ | Dichloroethane | 100 | 31 | 60 |
| $PhSiH_3$ | Ethyl acetate | 96 | 23 | 70 |
| $PhSiH_3$ | Dimethoxyethane | 100 | 6 | 90 |
| $PhSiH_3$ | THF | 100 | 3 | 93 |

**Note**. Reaction conditions: 3-methylbut-2-enyl benzoate (1 mmol) and silane (2 mmol) are stirred in the solvent (5 ml) in the presence of $Co(acac)_2$ (0.05 mmol) in oxygen atmosphere at room temperature for 12 h.

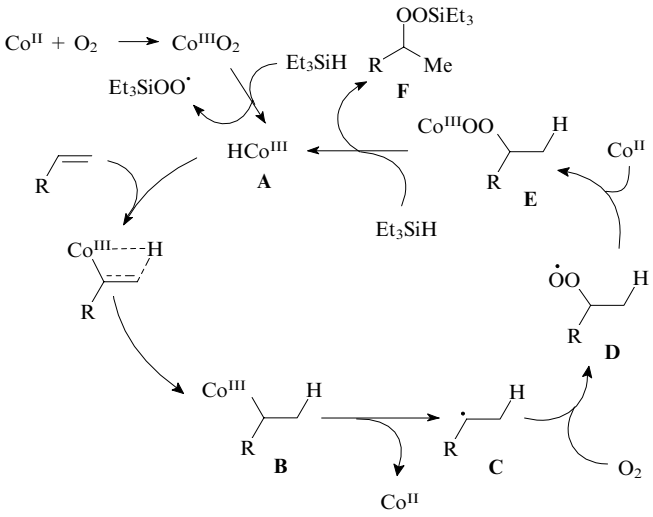
presence of phenylsilane results in alcohol **35** as the major product (Table 5).




Thus, $Co(acac)_2$-catalyzed reaction (2) carried out in THF in the presence of phenylsilane instead of triethylsilane can be recommended as a method of synthesis of alcohols from alkenes.

A number of studies on the mechanism of the Isayama – Mukaiyama reaction (Scheme 2) are available.[66, 120, 125]

Scheme 2




The first stage involves generation of $HCo^{III}$ (intermediate **A**) by the oxidation of $Co^{II}$ by oxygen followed by the interaction with $Et_3SiH$. Then, $HCo^{III}$ is added to the alkene double bond with the formation of intermediate **B**. Homolysis of the intermediate **B** is accompanied by generation of the C-centred radical **C** which adds an oxygen molecule to give the O-centred radical **D**. The interaction of radical **D** with $Co^{II}$ results in the $Co^{III}$-alkylperoxy complex **E** whose reaction with $Et_3SiH$ leads to the desired peroxysilane **F** and regeneration of $HCo^{III}$.

The Isayama – Mukaiyama reaction offers prospects for the synthesis of various (including functionalized) organic peroxysilanes with complex structures. The published data on the synthesis of organosilicon peroxides using the Isayama – Mukaiyama reaction are listed in Table 6.

The Isayama – Mukaiyama reaction is a key step in the synthesis of some cyclic peroxides with high antiparasitic

**Table 6**. Synthesis of peroxysilanes using the Isayama – Mukaiyama reaction (in 1,2-dichloroethane).

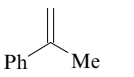
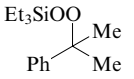
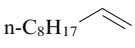
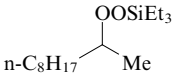
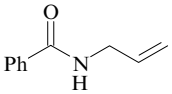
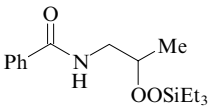
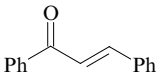
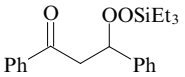
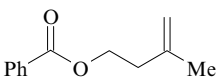
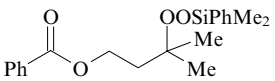
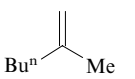
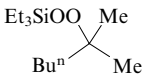
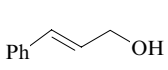
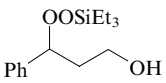
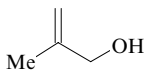
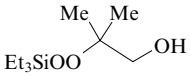
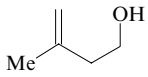
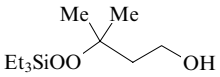
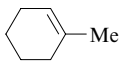
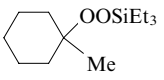
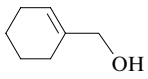
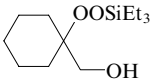
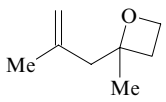
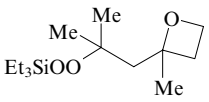
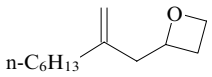
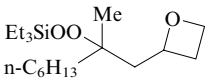
| Alkene | Silyl peroxide | Reaction conditions | Yield (%) | Ref. |
|---|---|---|---|---|
|  |  | $Co(modp)_2$, 5 h | 95 | 63 |
|  |  | $Co(modp)_2$, 12 h | 80 | 63 |
|  |  | $Co(modp)_2$, 24 h | 80 | 63 |
|  |  | $Co(modp)_2$, 12 h | 75 | 63 |
|  |  | $Co(modp)_2$, 2 h [a] | 72 | 65 |
|  |  | $Co(thd)_2$ | 80 | 120 |

**Table 6** (continued).

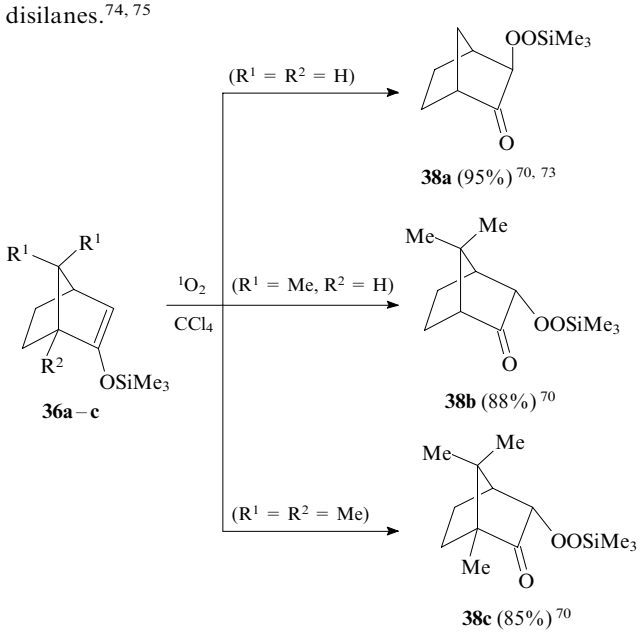
| Alkene | Silyl peroxide | Reaction conditions | Yield (%) | Ref. |
|---|---|---|---|---|
|  |  | $Co(thd)_2$ | 88 | 120 |
|  |  | $Co(thd)_2$ | 90 | 120 |
|  |  | $Co(acac)_2$ | 50 | 124 |
|  |  | $Co(thd)_2$ | 68 | 120 |
|  |  | $Co(thd)_2$ | 72 | 120 |
|  |  | $Co(acac)_2$ | 78 | 40 |
|  |  | $Co(acac)_2$ | 80 | 40 |

[a] $PhMe_2SiH$ was used as a reagent, in other cases — $Et_3SiH$.

activity, for example, plakinic acids (see below),[40,41] as well as the analogues of plakortin,[42] yingzhaosu C,[126,127] yingzhaosu A [130] and artemisinin.[128]

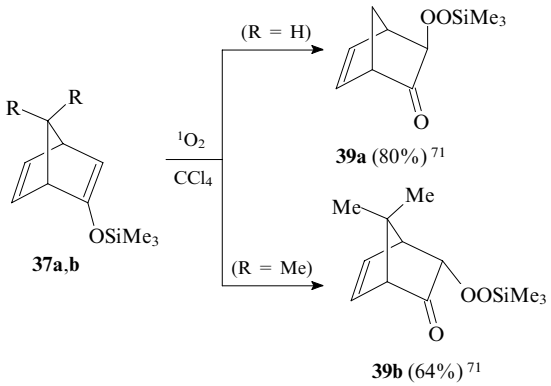
## IV. Synthesis of organosilicon peroxides using singlet oxygen

There are two main approaches to the synthesis of organosilicon peroxides using singlet oxygen. These are the reactions with enol silyl ethers [67–73,132–137] and with disilanes.[74,75]




$R^1$ = H: $R^2$ = H (**a**), Me (**b**); $R^1$ = $R^2$ = Me (**c**).

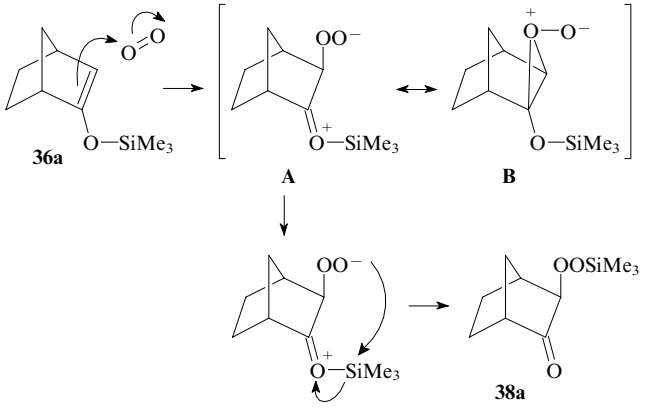
Reactions of singlet oxygen with enol silyl ethers **36a–c** and **37a,b** in aprotic solvents (carbon tetrachloride [70,71,73] and dichloromethane [72,137]) give the corresponding silylperoxy ketones **38a–c** and **39a,b** in yields up to 95%.



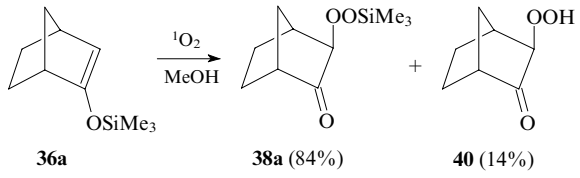

The proposed mechanism of the oxidation of silyl enolates is shown in Scheme 3 taking compound **36a** as an example.[70] In the first step, singlet oxygen adds to the double bond of ester **36a** to give the intermediates **A** and **B**, which undergo a rearrangement with transfer of the trimethylsilyl group to silylperoxy ketone **38a**.

Carrying out this reaction in protic solvents (for example, methanol) using (bicyclo[2.2.1]hept-2-en-2-yloxy)trimethylsilane (**36a**) as the starting compound allows one to obtain 3-(trimethylsilylperoxy)bicyclo[2.2.1]heptan-2-one (**38a**) and 3-hydroperoxybicyclo[2.2.1]heptan-2-one (**40**) as the major and side product, respectively.[70,73]

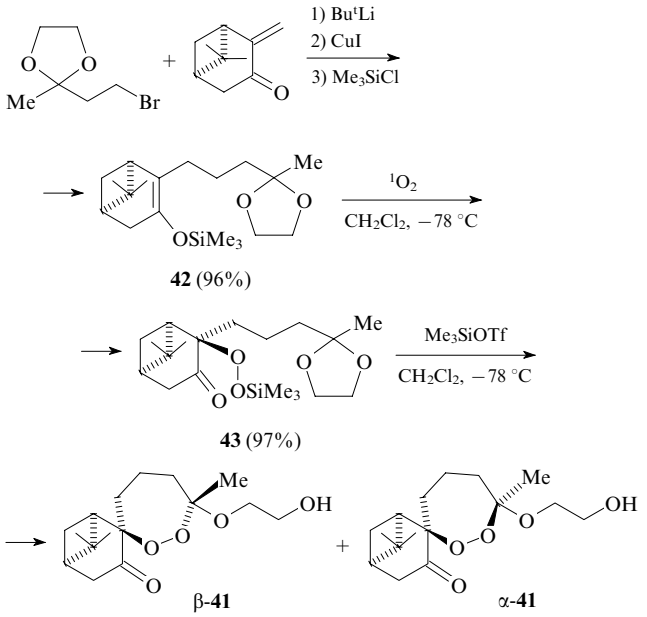
Scheme 3



The formation of hydroperoxide **40** can be explained by partial desilylation of silylperoxy ketone **38a** under the action of methanol.

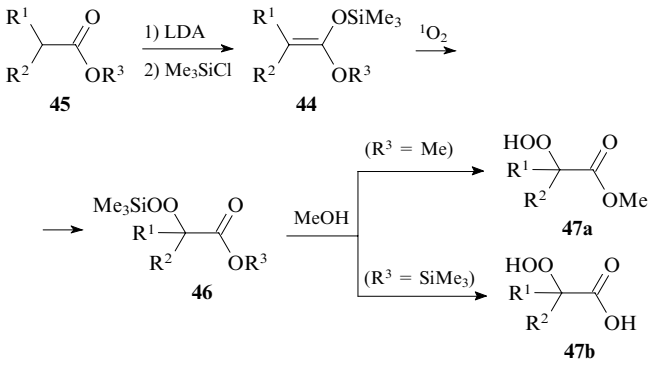


The synthesis of the cyclic peroxides **41** with high antimalarial activity was reported.[137] A key stage of the process is the reaction of singlet oxygen with compound **42** affording peroxysilane **43** whose treatment with $Me_3SiOTf$ results in the spiro-peroxides bearing the methyl group in α- and β-configurations (compounds α-**41** and β-**41**, respectively) in a 1 : 3 ratio and a total yield of 41%.



The antimalarial activity of cyclic peroxides **41** is comparable to that of artemisinin which is widely used in medical practice for malaria treatment.

Yet another type of reactions of singlet oxygen affording peroxysilanes is represented by its reactions with *O*-silylketenacetals **44** obtained by treatment of esters **45** with lithium diisopropylamide (LDA) followed by the interaction with trimethylsilane. This method makes it possible to synthesize esters **46** containing the silylperoxy group in α-position.[67, 132] Subsequent storage of peroxysilanes **46** in methanol at 0 °C for 12 h leads to hydroperoxides **47a** (R = Me) or hydroperoxy acids **47b** ($R^3 = SiMe_3$).

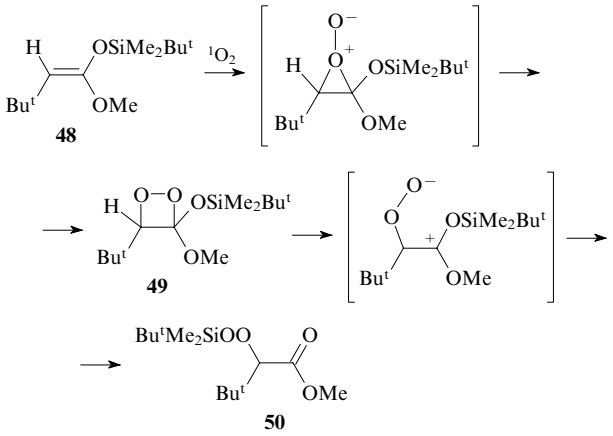


| $R^1$ | $R^2$ | $R^3$ | Yield (%) | | | Ref. |
|---|---|---|---|---|---|---|
| | | | **44** | **46** | **47** | |
| Me | Me | Me | 62 | 80 | 80 | 67 |
| $Bu^t$ | H | Me | 86 | 93 | 76 | 67 |
| $Bu^t$ | H | $SiMe_3$ | 72 | 90 | 87 | 132 |
| 1-Ad | H | Me | 84 | 80 | 69 | 67 |
| Ph | Ph | Me | 92 | 70 | 72 | 67 |

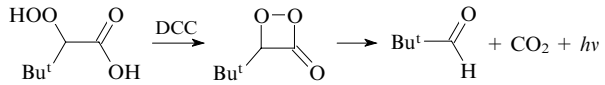
Ad is adamantyl.

Peroxysilanes **46** are synthesized in carbon tetrachloride at 0 °C with the addition of tetraphenylporphyrin (TPP). Singlet oxygen is generated by irradiation of a stream of dry oxygen with a 400 W Na-lamp.[67]

Peroxysilylation of (*E*)-*tert*-butyl(dimethyl)silyl-(1-methoxy-3,3-dimethylbut-1-enyl) ester (**48**) by singlet oxygen proceeds *via* formation of 1,2-dioxetane **49**. Compound **49** is unstable and undergoes rearrangement to methyl 2-[*tert*-butyl(dimethyl)silyl]peroxy-3,3-dimethylbutanoate (**50**).[68, 133]

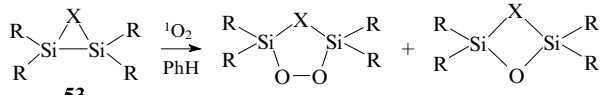


Hydroperoxy acid **47b** is a convenient system for chemoluminescence studies. Under the action of 1,3-dicyclohexylcarbodiimide (DCC), compound **47b** is transformed to peroxylactone (4-*tert*-butyl-1,2-dioxetan-3-one, **51**) whose decomposition with the formation of pivalaldehyde (**52**) and $CO_2$ is accompanied by chemiluminescence.[134, 135]



47b 51 52

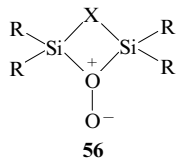
The interaction of cyclic disilanes **53** with singlet oxygen leads to cyclic organosilicon peroxides **54**, products of oxygen insertion into the Si—Si bonds. Stable siletanes **55** (Mes = 2,4,6-$Me_3C_6H_2$) are formed as side products.[74, 75]



53 54 55

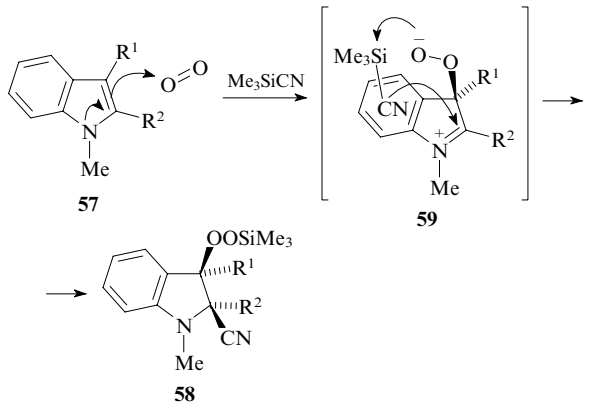
| R | X | Yield of **54** (%) | Ref. |
|---|---|---|---|
| 2,6-$Me_2C_6H_3$ | O | 43 | 74 |
| 2,6-$Et_2C_6H_3$ | O | 60 | 74 |
| 2,6-$Pr^i{}_2C_6H_3$ | O | 71 | 74 |
| Mes | O | 40 | 74 |
| Mes | $CH_2$ | 52 | 75 |

The reaction is carried out in benzene at 15 °C with the addition of tetraphenylporphyrin. Singlet oxygen is generated by irradiation of dry bubbling oxygen with two 500 W halogen lamps.[75] It is assumed that the reaction begins with insertion of singlet oxygen into the Si—Si bond resulting in the intermediate **56** which subsequently undergoes a rearrangement into cyclic peroxysilane **54**.[74]



56

Reactions of singlet oxygen with *N*-methylindoles **57** in MeCN at −30 °C in the presence of trimethylsilyl cyanide yield 3-trimethylsilylperoxy-2-cyanoindolines **58**.[138] Trimethylsilyl cyanide is an effective scavenger of dipolar peroxide intermediates **59**.



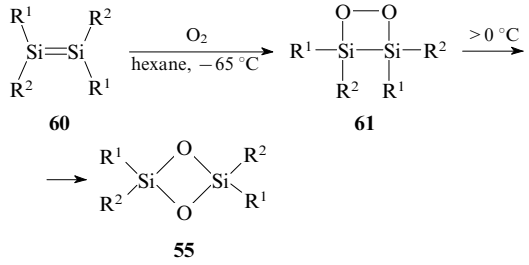
57 59 58

$R^1$ = Me, $R^2$ = H (70%); $R^1$ = $Pr^i$, $R^2$ = Me (45%).

## V. Other methods of synthesis of organosilicon peroxides

This Section concerns a number of synthetic approaches to peroxysilanes that are of limited use. In these methods, peroxysilanes are unstable, or play the role of intermediate products, or are formed in low yields.

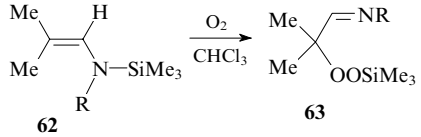
The oxidation of tetrasubstituted disilenes **60** by atmospheric oxygen in hexane at −65 °C gives unstable 1,2-dioxadisiletanes **61**[139, 140] (average half-life is 4.5 h in solution at 25 °C). Thermal rearrangement of compounds **61** leads to 1,3-dioxadisiletanes **55** (X = O), which are stable at room temperature.



60 61 55

| $R^1$ | $R^2$ | Yield of **61** (%) |
|---|---|---|
| 2,6-$Me_2C_6H_3$ | 2,6-$Me_2C_6H_3$ | >80 |
| Mes | $Bu^t$ | 91 |
| Mes | Mes | 91 |
| 2,6-$Me_2$-4-$Bu^tC_6H_2$ | 2,6-$Me_2$-4-$Bu^tC_6H_2$ | ~80 |

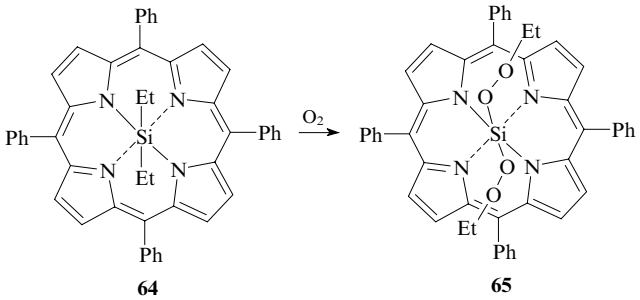
Bubbling air through solutions of *N*-trimethylsilyl-*N*-alkylidenamines **62** in chloroform or dioxane results in α-trimethylsilylperoxy-*N*-alkylaldimines **63**.[141]



62 63

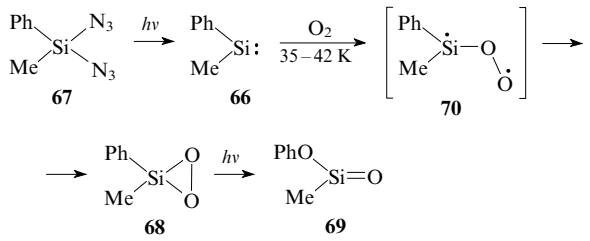
R = Me (71%), Et (84%).

The reaction of diethylsilicon tetraphenylporphyrinate (**64**) with atmospheric oxygen in the dark leads to bis(ethylperoxy)silicon tetraphenylporphyrinate **65**.[142] The reaction was carried out in an NMR tube. Through a solution of Si(TPP)$Et_2$ (7.0 mg) in $C_6D_6$ (0.5 ml), oxygen was bubbled for 5 min. Then, the tube was sealed and kept in the dark. The course of the reacton was periodically monitored by $^1$H NMR spectroscopy. The conversion of porphyrin **64** was completed in 25 days. The yield of compound **65** was 90%.

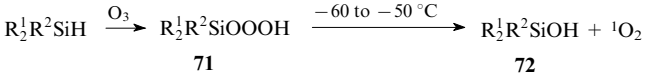


64 65

Methylphenylsilylene **66** obtained from diazide **67** reacts with oxygen in an argon matrix at 35–42 K to give an unstable 3-methyl-3-phenyl-3-dioxasilirane **68**, which undergoes rearrangement to methylphenyloxysilanone **69**. It seems likely that the reaction proceeds through the formation of the methylphenylsilylperoxy biradical **70**.[143–146]



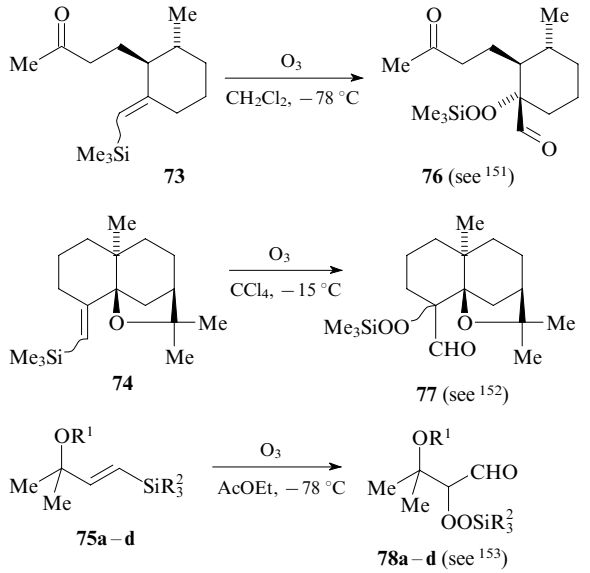
The ozonolysis of trialkyl(aryl)silanes at −78 °C leads to trialkyl(aryl)silyl hydrotrioxides **71**. These compounds are unstable and decompose in the temperature range from −60 to −50 °C to trialkyl(aryl)silanols **72** and singlet oxygen.[147–150]



| $R^1$ | $R^2$ | Ref. |
|---|---|---|
| Me | Me | 150 |
| Et | Et | 148 |
| Me | Ph | 149 |
| Ph | Ph | 150 |
| $Bu^n$ | $Bu^n$ | 147 |
| Me | 4-$MeC_6H_4$ | 149 |

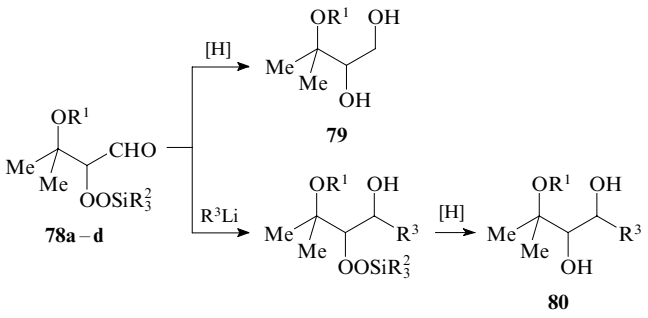
Silyl hydrotrioxides **71** were characterized by $^1H$, $^{13}C$, $^{17}O$ and $^{29}Si$ NMR spectroscopies.

Reactions of trialkylvinylsilanes **73**–**75** with ozone result in α-trialkylsilylperoxyaldehydes **76**–**78**.[151–154] The process is carried out in aprotic solvents ($CCl_4$, $CH_2Cl_2$, AcOEt) at temperatures from −78 to −15 °C.

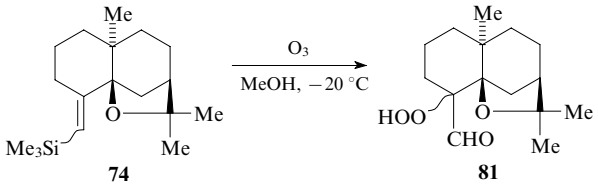


| Compound | $R^1$ | $R^2_3$ | Yield (%) |
|---|---|---|---|
| **78a** | H | $Bu^tMe_2$ | 73 |
| **78b** | H | $Pr^i_3$ | 80 |
| **78c** | $SiMe_3$ | $Pr^i_3$ | 75 |
| **78d** | $SiMe_3$ | $Bu^tMe_2$ | 67 |

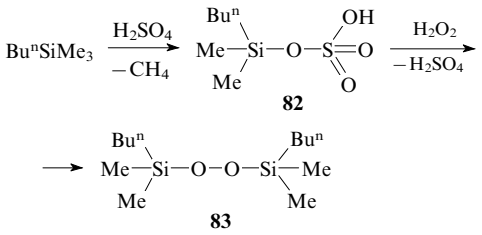
Direct reduction (or reduction with pre-alkylation) of α-trialkylsilylperoxyaldehydes **78a**–**d** leads to the triol derivatives **79**, **80**.[153, 154]



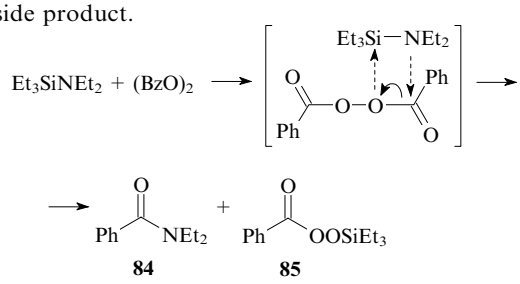
Ozonolysis of trialkylvinylsilane **74** in methanol at 20 °C affords the hydroperoxide **81** as the major product in a yield of 67%.[152]



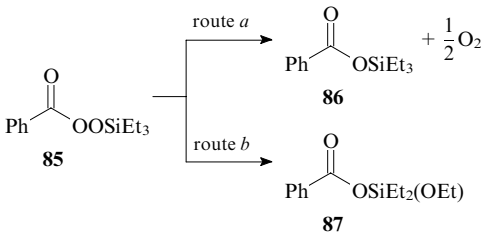
The reaction of n-butyltrimethylsilane with sulfuric acid gives butyldimethyl sulfate **82** and methane.[106] Subsequent treatment of sulfate **82** with hydrogen peroxide leads to sulfuric acid and bis(butyldimethylsilyl) peroxide **83**.



The reaction of triethylsilyldiethylamine with dibenzoyl peroxide in benzene at room temperature is completed in two days.[105] The major reaction product is diethylbenzamide (**84**, yield 72%), triethylsilicon perbenzoate (**85**) being a side product.



Triethylsilicon perbenzoate (**85**) is unstable and decomposes following two routes, *a* and *b*, to triethylsilyl benzoate (**86**) and diethyl(ethoxy)silyl benzoate (**87**), respectively.



Route *a* is of minor importance. Route *b* involving a heterolytic rearrangement is the main route which results in diethyl(ethoxy)silyl benzoate (**87**).[105]

## VI. Reactions of organosilicon peroxides

Organosilicon peroxides react with both nucleophilic and electrophilic agents. A nucleophile may attack a number of reactive centres, *e.g.*, the silicon atom, the peroxide oxygen atom and the carbon atom bound to the silicon atom. The reactions with electrophiles involve the peroxide oxygen atoms. The redox reactions are typical of peroxysilanes similarly to all peroxides.

Bis(trimethylsilyl) peroxide (BTMSPO, **5a**) is used in organic synthesis to obtain the trimethylsilyl ethers **88** from alkyl-,[34, 155–161] vinyl-,[34, 35, 162, 163] aryl-[33, 34, 164] and hetaryl-substituted[3, 34, 165] organolithium or organomagnesium compounds. Acid hydrolysis of compounds **88** leads to the corresponding alcohols.

$$\underset{\mathbf{5a}}{Me_3SiOOSiMe_3} + RM \longrightarrow \underset{\mathbf{88}}{ROSiMe_3} + MOSiMe_3,$$

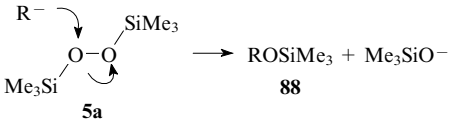
$$\underset{\mathbf{88}}{ROSiMe_3} \xrightarrow{H^+,\ H_2O} ROH + Me_3SiH,$$

R = Alk, $CH_2$=CH, Ar, Het; M = Li, MgCl.

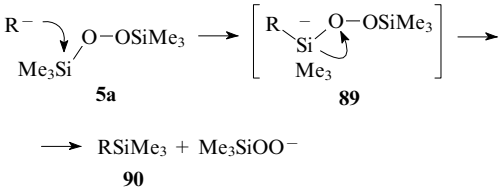
Reactions of carbanions with BTMSPO do not always result in the trimethylsilyl ethers **88**. There are three main directions of nucleophilic attack by the carbanion;[155, 156, 160] depending on the direction, different products are formed.

The carbanion R can attack:

*a*) an oxygen atom of the O–O unit to give the trimethylsilyl ether **88** and the trimethylsilanolate anion:



*b*) a silicon atom with the formation of intermediate **89**, which undergoes rearrangement to trimethylalkylsilane **90** and the peroxide anion:

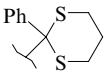
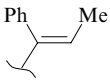
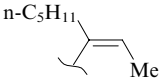
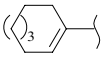


*c*) the methyl carbon atom to yield a product of methylation of the carbanion, dimethylsilanone and the trimethylsilanolate anion.



The available published data mainly concern the reactions of organolithium and organomagnesium compounds with BTMSPO resulting in trimethylsilyl ethers **88** (route *a*) as major products (Table 7).[33–35, 158, 159, 161–165] Trimethylalkylsilanes **90** are formed as side products of reaction (3) proceeding by route *b* (see Table 7).

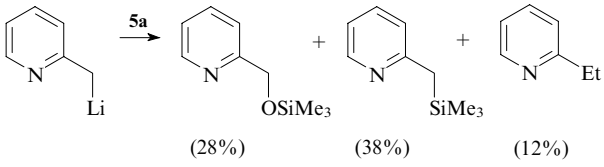
**Table 7**. Products of reaction (3).

| R | M | Yield (%) | | Ref. |
|---|---|---|---|---|
| | | **88** | **90** | |
| $Bu^n$ | Li | 89 | traces | 34 |
| n-$C_5H_{11}$ | MgBr | 70 | – | 34 |
| Ph | Li | 86 | – | 33 |
| 4-$MeOC_6H_4$ | Li | 61 | – | 33 |
| 3-Th [a] | Li | 65 | – | 33 |
| 2-Th | Li | 53 | 30 | 34 |
| 9-Fluorenyl | Li | 75 | – | 33 |
|  | Li | – | 56 | 34 |
| $CH_2$=CH | Li | 10 | 42 | 34 |
| | MgBr | 53 | 0 | 34 |
|  | Li | 70 | – | 35 |
|  | Li | 82 | – | 35 |
| PhCHSMe | Li | 45 | 30 | 158 |
| $Me_3SiCHCN$ | Li | 48 | 5 | 158 |
| $Me_3SiCHSMe$ | Li | 75 | 5 | 158 |
|  | Li | 52 | – | 162 |

**Note**. From this point on, the dash in the table means that the yield was not specified in the original article. [a] Th is thienyl.

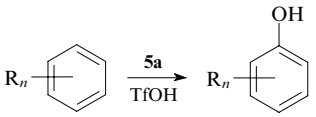
$$RM + \underset{\mathbf{5a}}{} \longrightarrow \underset{\mathbf{88}}{ROSiMe_3} + \underset{\mathbf{90}}{RSiMe_3} \qquad (3)$$

As a rule, the reactions of organomagnesium compounds are characterized by higher selectivity than those of organolithium compounds. That is why the trimethylsilyl ethers **88** are formed in higher yields.[34] It was shown[34, 155] that alkyltrimethylsilanes **90** can be formed as the major products, too. For example, in the reaction of lithium phenylacetylenide with BTMSPO, the product of trimethylsilylation was isolated in a yield of 40% and no formation of trimethylsilyl ether was observed.[34] If R = 2-pyridylmethyl,[155] the reaction proceeds *via* all three routes.



(28%) (38%) (12%)

Reactions of BTMSPO with aromatic hydrocarbons (benzene, toluene, *o*-xylene, naphthalene and chlorobenzene) acting as nucleophiles in the presence of trifluoromethanesulfonic acid result in isomeric mixtures of phenols in yields from 71% to 94%.[166]



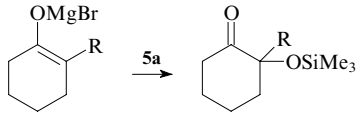
$R_n$ = H, Me, *o*-$Me_2$, Cl, benzo.

In reactions of organosilicon peroxides with alkoxide anions, the nucleophile attacks the silicon atom. For example, the reaction of compound **5a** with a suspension of sodium ethoxide in toluene at room temperature takes 14 h to complete and gives ethyltrimethylsilyl ether and trimethylsilylsodium peroxide.[45]

$$Me_3SiOOSiMe_3 + NaOEt \longrightarrow EtOSiMe_3 + NaOOSiMe_3$$

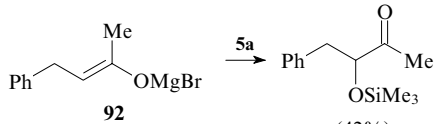
**5a**

Magnesium bromide enolates **91**–**93** react with BTMSPO to give the corresponding 2-trimethylsilyloxycarbonyl compounds.[34]

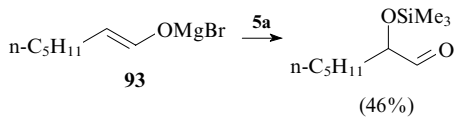


**91**

R = H (61%), Me (40%).

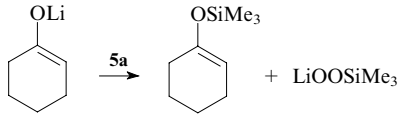


**92** (42%)



**93** (46%)

The reaction of lithium cyclohexen-1-enolate with silyl peroxide **5a** proceeding under similar conditions results in trimethylcyclohexenyloxysilane.[34]



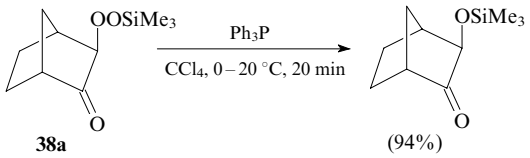
Bis(trimethylsilyl) peroxide (**5a**) readily reacts with such nucleophiles as sulfides, sulfoxides, phosphites[5,45] and phosphines.[5,45,167,168] As a result, the nucleophilic agents (Nu) are oxidized to the corresponding oxides (NuO) and BTMSPO is transformed to hexamethyldisiloxane. As a rule, the oxidation is carried out at room temperature and the reaction time varies from one hour to a few days.[45]

$$Me_3SiOOSiMe_3 \xrightarrow{Nu} Me_3SiOSiMe_3 + NuO,$$

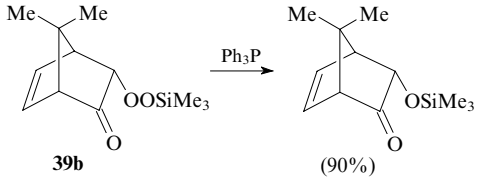
**5a**

Nu = $R_2S$, $R_2SO$, $(RO)_3P$, $R_3P$ (R = Alk, Ar).

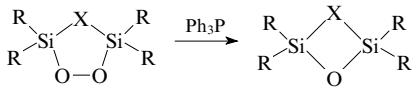
The reduction of organosilicon peroxides with complex structures containing the SiOOSi and SiOOC units, namely, compounds **38a**,[70] **39b**,[70] **54**[74,75] and **94**–**97**[77,78,153,169] was reported. The most widely used reducing agents include phosphines $Ph_3P$ and $Me_3P$.



**38a** (94%)

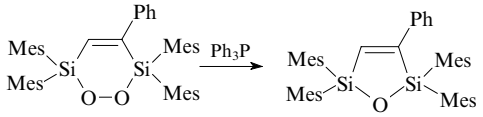


**39b** (90%)

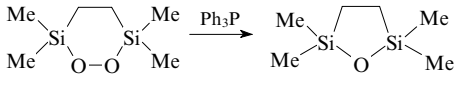


**54** **55**

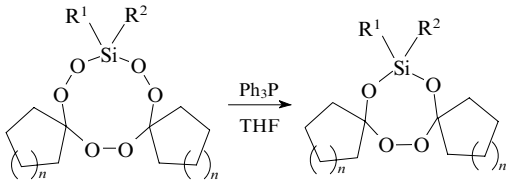
X = O: R = Mes (83%), 2,6-$Me_2C_6H_3$ (96%);[74]
X = $CH_2$, R = Mes (71%).[75]



**94** (50%)[169]

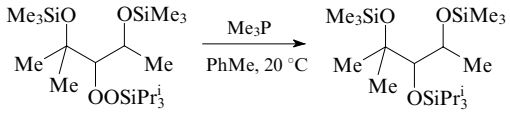


**95** (57%)[77]



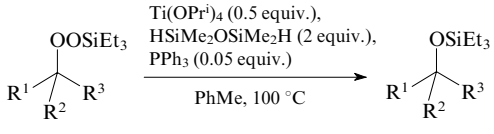
**96** (67%–91%)[78]

*n* = 2, 3: $R^1 = R^2$ = Me, Et; *n* = 8: $R^1 = R^2$ = Me, Et, Ph;
$R^1$ = Me: $R^2$ = CH=$CH_2$, cyclo-$C_6H_{11}$, $(CH_2)_3CO_2Et$.



**97** (61%)[153]

A convenient method of reduction of the SiOOC peroxides **98** to alkoxysilanes **99** using catalytic amounts of triphenylposphine was developed.[170]

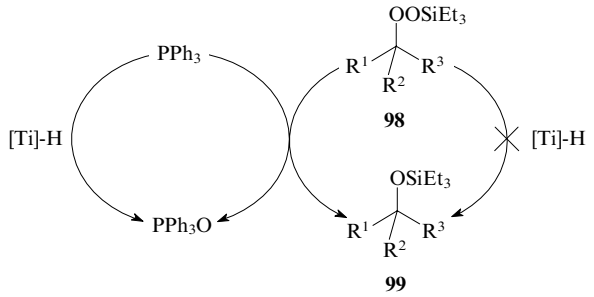


**98** **99**

$R^1$ = Ph: $R^2$ = Me, $R^3 = Pr^i$ (73%); $R^2$ = Et, $R^3$ = H (73%);
$R^1$ = Me, $R^2$–$R^3$ = $(CH_2)_5$ (46%); $R^1$ = H, $R^2$–$R^3$ = $(CH_2)_n$ [*n* = 7 (66%), 11 (79%)].

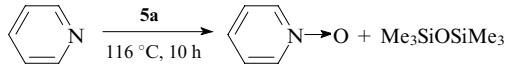
In the course of reduction, triphenylphosphine is regenerated from triphenylphosphine oxide under the action of the $Ti(OPr^i)_4 - HSiMe_2OSiMe_2H$ system (Scheme 4).

Scheme 4

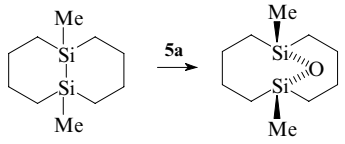



A peculiar feature of the method is that the reducing agent generated from the titanium compounds selectively reduces triphenylphosphine oxide and does not affect the silyl peroxide **98**.

As a rule, reactions of silyl peroxides with amines proceed until formation of complexes,[104, 171, 172] but in some cases the amine is oxidized to the N-oxide. For instance, the reaction of BTMSPO with an excess of pyridine at 116 °C affords pyridine N-oxide and hexamethyldisiloxane after 10 h.[45]



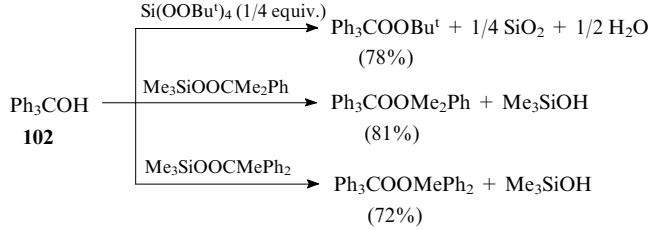

The oxidation of *cis*- and *trans*-9,10-dimethyl-9,10-disiladecalins (**100**) by bis(trimethylsilyl) peroxide at 80 °C over a period of 50 h results in *cis*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (**101**), a product of the oxygen insertion into the Si—Si bond.[173]

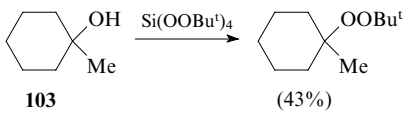



**100** *cis*-**101**

The electron pairs of the peroxide oxygen atom are involved in the reactions of organosilicon peroxides with electrophiles. The simplest case is acid-catalyzed hydrolysis or alcoholysis of silicon-containing peroxides.

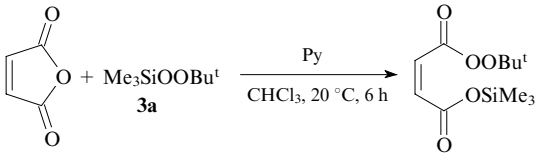
Reactions of tertiary alcohols, *e.g.*, triphenylmethanol (**102**) and 1-methylcyclohexanol (**103**), with various silyl peroxides in acetic acid in the presence of $H_2SO_4$ lead to the corresponding dialkyl peroxides.[174]



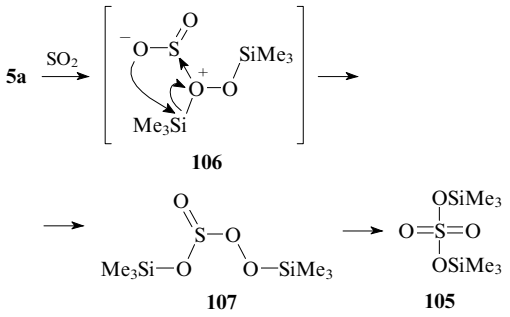

**103** (43%)

*tert*-Butyl(trimethylsilyl) peroxide (**3a**) reacts with maleic anhydride to give trimethylsilyl-(*Z*)-4-(*tert*-butylperoxy)-4-oxobut-2-enoate (**104**). The process is carried out in the presence of pyridine at 20 °C.[175]



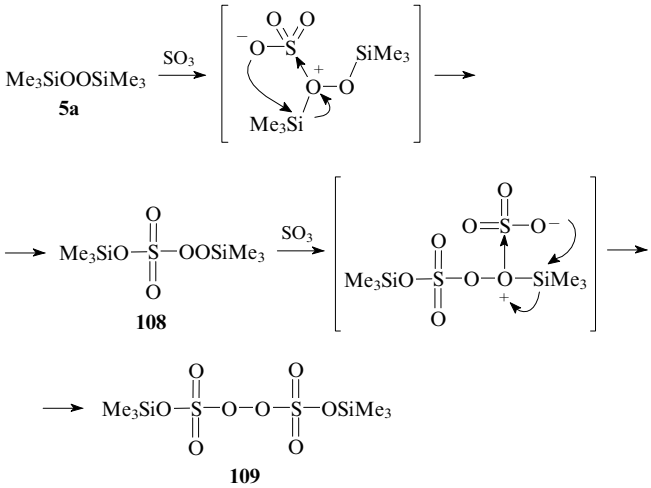

**104** (83%)

The reaction of bis(trimethylsilyl) peroxide (**5a**) with liquid sulfur dioxide at −20 °C affords bis(trimethylsilyl) sulfate (**105**) after 2 h.[45]

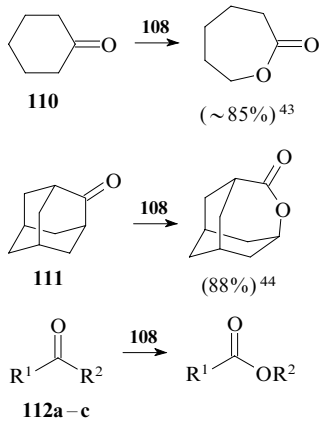



Sulfur dioxide is coordinated to the lone electron pair of the peroxide group of BTMSPO with the formation of complex **106** whose rearrangement gives trimethylsilyl(trimethylsilyloxy) sulfite (**107**). The latter transforms to sulfate **105** *via* intramolecular oxidation.[5]

Sulfur trioxide also reacts with BTMSPO (**5a**). The process carried out in $CH_2Cl_2$ at −30 °C results in trimethylsilyl(trimethylsilyloxy) sulfate (**108**).[176] Subsequent treatment of peroxysulfate **108** with $SO_3$ yields bis(trimethylsilyl) peroxydisulfate (**109**).[5]

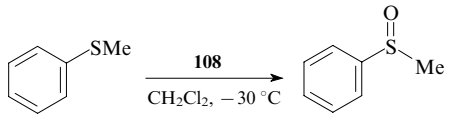


Trimethylsilyl(trimethylsilyloxy) sulfate (**108**) is an efficient reagent for the Bayer–Villiger oxidation of ketones (*e.g.*, compounds **110**–**112**) to the corresponding lactones or esters.[43,44] The process is carried out in dichloromethane at −30 °C; the reaction time varies from 45 min to a few hours depending on the ketone structure.

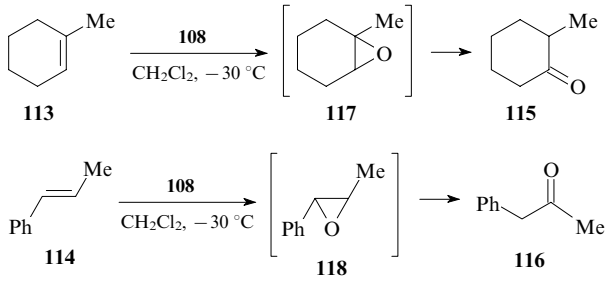



$R^1 = R^2 = Pr^n$ (**a**, 96%);[44]
$R^2$ = Ph: $R^1$ = Me (**b**, ~74%),[43] Ph (**c**, 83%).[44]

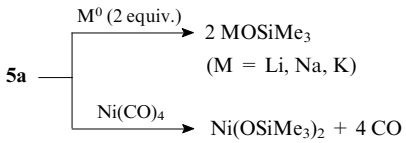
Methyl phenyl sulfide is oxidized to methyl phenyl sulfoxide under the action of trimethylsilyl(trimethylsilyloxy) sulfate (**108**) under very mild conditions.[43]



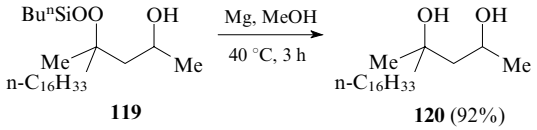

Compound **108** oxidizes the alkenes **113** and **114** to the corresponding ketones **115** and **116** *via* the formation of oxiranes **117** and **118**, respectively; the reagent itself is reduced to bis(trimethylsilyl) sulfate **105**. As a rule, the reactions are carried out in dichloromethane in the presence of catalytic amounts of a ketone (acetone or cyclohexanone) at temperatures from −70 to −30 °C over a period of a few hours.[43]




Alkali metals (Li, Na, K) in the form of suspension in toluene quantitatively reduce bis(trimethylsilyl) peroxide (**5a**) at 20 °C within 1–2 h to give the alkali metal trimethylsilanolate.[45] Treatment of BTMSPO with tetracarbonyl nickel in petroleum ether at 20–40 °C for 30 min leads to nickel(II) trimethylsilanolate and carbon monoxide.[45]




Under the action of the Mg–MeOH system at 40 °C, peroxysilane **119** is reduced to diol **120** after 3 h in high yield.[177]




In addition, reactions of bis(trimethylsilyl) peroxide (**5a**) with lead tetraacetate and chromium trioxide proceed with the release of molecular oxygen.[45]

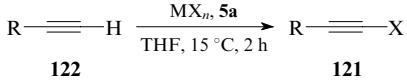
$$\mathbf{5a} + Pb(OAc)_4 \longrightarrow 2\,Me_3SiOAc + Pb(OAc)_2 + O_2,$$

$$3\,\mathbf{5a} + 2\,CrO_3 + 6\,AcOH \longrightarrow$$
$$\longrightarrow 3\,Me_3SiOSiMe_3 + 2\,Cr(OAc)_3 + 3\,H_2O + 3\,O_2.$$

Concentrated hydrogen peroxide undergoes transformation to peroxonium hexafluoroantimonate ($H_3O_2^+SbF_6^-$) under the action of the superacid $HSbF_6$. A similar reaction also occurs in the case of BTMSPO. In this reaction, replacement of hydrogen peroxide by bis(trimethylsilyl) peroxide (**5a**) makes it possible to carry out the process under very mild conditions; the released water is bound to the complex $H_3O_2^+SbF_6^-$ (Ref. 178).

$$\mathbf{5a} + 3\,HF + SbF_5 \xrightarrow{HF,\ -70\ ^\circ C} H_3O_2^+SbF_6^- + 2\,Me_3SiF.$$

Compound **5a** is used for the synthesis of alkynyl halides and alkynyl cyanides **121**. The method is based on the interaction of the terminal alkynes **122** with copper or zinc salts in the presence of equivalent quantities of BTMSPO in THF at 15 °C.[179]

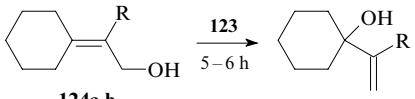



| R | X | $MX_n$ | Yield (%) |
|---|---|---|---|
| $Pr^n$ | I | $ZnI_2$ | 45 |
| Ph | I | $ZnI_2$ | 85 |
| $Me_3Si$ | I | CuI | 80 |
| $Me_3Si$ | Br | CuBr | 60 |
| Ph | CN | CuCN | 65 |

This reaction is a modification of an earlier approach based on the interaction of alkynyllithium with zinc iodide in the presence of BTMSPO.[180]

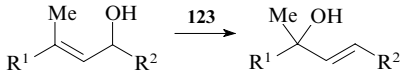
A catalyst **123** prepared from $VO(acac)_2$ and bis(trimethylsilyl) peroxide (**5a**) was reported.[181] In the presence of compound **123**, the primary and secondary allyl alcohols **124** and **125**, respectively, isomerize to the corresponding tertiary allyl alcohols **126**, **127** in dichloromethane at 25 °C

[0.3 mmol of BTMSPO and 0.1 mmol of $VO(acac)_2$ per mmol of alcohol are used].



**124a,b** **126a,b**

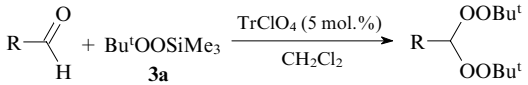
R = H (**a**, 92%), Me (**b**, 85%).



**125a–c** **127a–c**

| Compound **127** | $R^1$ | $R^2$ | Time /h | Yield (%) |
|---|---|---|---|---|
| **a** | Me | Me | 1 | 97 |
| **b** | n-$C_6H_{13}$ | H | 24 | 53 |
| **c** | Me | n-$C_6H_{13}$ | 1 | 76 |

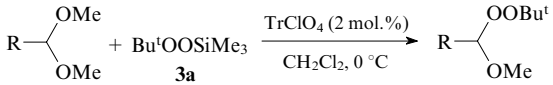
Aliphatic and aromatic aldehydes **128** react with *tert*-butyl(trimethylsilyl) peroxide (**3a**) to give bis(*tert*-butyl peroxides) **129** in yields of up to 95%. The reactions are carried out in dichloromethane in the temperature range from −78 to 0 °C in the presence of 5 mol.% of trityl perchlorate ($TrClO_4$).[37]



**128** **3a** **129**

| R | Time /h | Temperature /°C | Yield (%) |
|---|---|---|---|
| $CH_2{=}CH(CH_2)_8$ | 3 | −45 | 92 |
| Ph | 12 | −78 | 88 |
| 2-$BrC_6H_4$ | 2.5 | −45 | 89 |
| 4-$MeSC_6H_4$ | 12 | −78 | 78 |
| $Ph(CH_2)_2$ | 0.15 | −45 | 95 |
| $BnO(CH_2)_2$ | 0.15 | 0 | 72 |

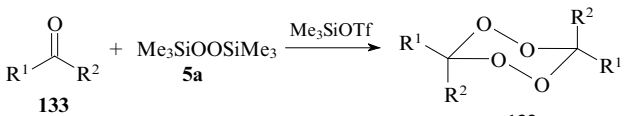
Acetals **130** are converted to methoxy peroxides **131** in high yields under the action of *tert*-butyl(trimethylsilyl) peroxide (**3a**) in dichloromethane in the presence of $TrClO_4$ (2 mol.%) at 0 °C.[182]



**130** **3a** **131**

| R | Yield (%) |
|---|---|
| n-$C_8H_{17}$ | 90 |
| n-$C_9H_{19}$ | 85 |
| $CH_2{=}CH(CH_2)_8$ | 86 |
| Bn | 86 |
| $Ph(CH_2)_2$ | 90 |
| PhCHMe | 88 |

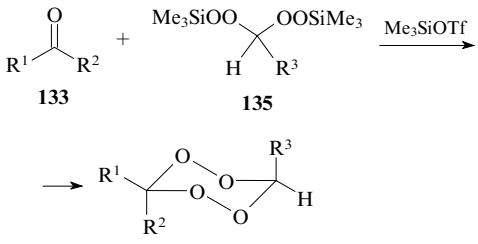
Symmetric 1,2,4,5-tetraoxanes **132** are obtained in moderate or high yields by the reactions of carbonyls **133** with bis(trimethylsilyl) peroxide (**5a**) in the presence of equivalent amounts of trimethylsilyl trifluoromethanesulfonate. The reactions are carried out in acetonitrile at 0 °C[183] or in $CH_2Cl_2$ at −70 °C.[184]



**133** **5a** **132**

| $R^1$ | $R^2$ | Yield (%) | Ref. |
|---|---|---|---|
| n-$C_9H_{19}$ | H | 51 | 183 |
| n-$C_7H_{15}$ | H | 57 | 183 |
| Ph | H | 60 | 184 |
| | | 46 | 183 |
| Me | Me | 95 | 183 |
| $(CH_2)_5$ | | 92 | 183 |

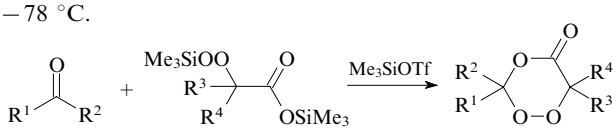
Asymmetric 1,2,4,5-tetraoxanes **134** are synthesized by the reactions of geminal bis(trimethylsilyl) peroxides **135** with ketones **133** in the presence of $Me_3SiOTf$.[114] The yields of the tetraoxanes **134** varied from 14% to 73% depending on the structures of starting compounds. Bis(trimethylsilyl) peroxides **135** are obtained by the interaction of geminal bishydroperoxides with *N*,*O*-bis(trimethylsilyl)acetamide in yields of 50%–67%.[114]



**133** **135** **134**

| $R^1$ | $R^2$ | $R^3$ | Yield (%) |
|---|---|---|---|
| Me | Me | Ph | 26 |
| Ph | H | n-$C_7H_{15}$ | 43 |
| 4-$FC_6H_4$ | H | cyclo-$C_6H_{11}$ | 53 |
| $(CH_2)_5$ | | Ph | 33 |
| $(CH_2)_5$ | | n-$C_7H_{15}$ | 33 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | Ph | 14 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | n-$C_7H_{15}$ | 44 |

The reaction of ketones **133** with trimethylsilyl-α-[(trimethylsilyl)peroxy]alkanoates **136** catalyzed by $Me_3SiOTf$ results in 1,2,4-trioxan-5-ones **137** also containing peroxide rings.[36,69] The process is carried out in dichloromethane at −78 °C.

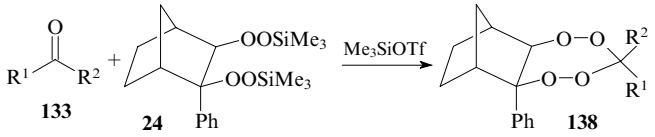


**133** **136** **137**

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield (%) | Ref. |
|---|---|---|---|---|---|
| Me | Me | H | $Bu^t$ | 45 | 36 |
| Me | Me | H | 1-Ad | 76 | 36 |
| Me | Me | $(CH_2)_5$ | | 78 | 69 |
| $(CH_2)_5$ | | H | $Bu^t$ | 90 | 36 |
| $(CH_2)_5$ | | H | 1-Ad | 91 | 36 |
| $(CH_2)_5$ | | $(CH_2)_5$ | | 93 | 69 |
| see [a] | | $(CH_2)_5$ | | 91 | 69 |
| see [a] | | H | 1-Ad | 81 | 36 |

[a] The ketone **133** is adamantan-2-one.

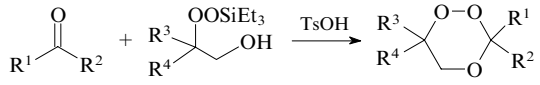
$Me_3SiOTf$ is also used as catalyst in the synthesis of 1,2,4,5-tetraoxepanes **138** from 1,2-bis(trimethylsilyl) peroxide **24** and carbonyls **133**.[111, 112] The reactions are carried out in $CH_2Cl_2$ at $-70$ °C using 0.6 mol of the triflate per mol of peroxide **24**.




**133** **24** **138**

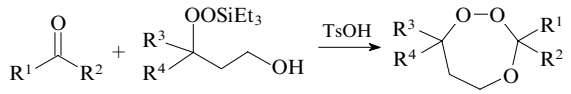
| $R^1$ | $R^2$ | Yield (%) |
|---|---|---|
| Ph | H | 23 |
| 4-$FC_6H_4$ | H | 13 |
| cyclo-$C_6H_{11}$ | H | 12 |
| $(CH_2)_5$ | | 19 |

Cyclization of aldehydes and ketones **133** with substituted 2-triethylsilylperoxyethanols **139** or 3-triethylsilylperoxypropan-1-ols **140** in the presence of *p*-toluenesulfonic acid (TsOH) results in 1,2,4-trioxanes **141**[120, 122] and 1,2,4-trioxepanes **142**,[121, 124] respectively. The starting alcohols **139** and **140** are synthesized by the Isayama – Mukaiyama reaction.




**133** **139** **141**

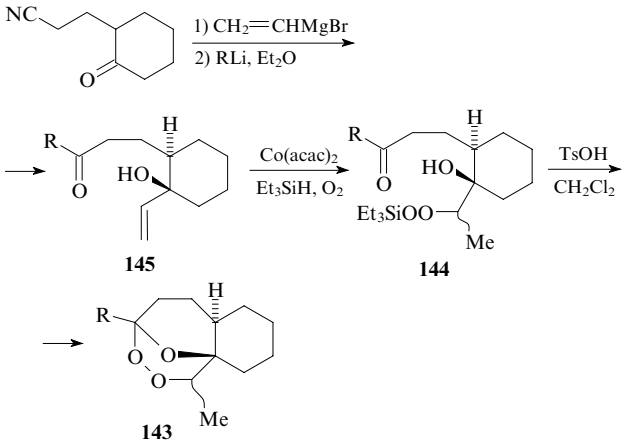
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield (%) | Ref. |
|---|---|---|---|---|---|
| H | Ph | Me | Me | 65 | 122 |
| H | 4-$O_2NC_6H_4$ | Me | Me | 40 | 122 |
| H | 4-$FC_6H_4$ | Me | Me | 90 | 122 |
| Me | 4-$FC_6H_4$ | Me | Me | 42 | 122 |
| Me | Me | $(CH_2)_5$ | | 85 | 120 |
| Me | 4-$F_3CC_6H_4$ | $(CH_2)_5$ | | 61 | 120 |
| $(CH_2)_5$ | | Me | Me | 53 | 122 |
| $(CH_2)_4$ | | Me | Ph | 42 | 122 |
| $(CH_2)_5$ | | Me | Ph | 54 | 122 |
| $(CH_2)_{11}$ | | $(CH_2)_5$ | | 40 | 120 |




**133** **140** **142**

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield (%) | Ref. |
|---|---|---|---|---|---|
| H | Me | Ph | H | 75 | 121 |
| H | $Pr^n$ | Ph | H | 70 | 121 |
| H | $Pr^i$ | Ph | H | 63 | 121 |
| H | 4-$MeO_2CC_6H_4$ | Me | Me | 90 | 124 |
| H | PhCH=CH | Me | Me | 83 | 124 |
| Me | Me | Ph | H | 71 | 121 |
| Me | 4-$EtO_2CC_6H_4$ | Me | Me | 91 | 124 |
| $Bu^n$ | $Bu^n$ | Me | Me | 95 | 124 |
| n-$C_6H_{13}$ | $MeO_2C(CH_2)_2$ | Me | Me | 90 | 124 |
| $(CH_2)_6$ | | Ph | H | 75 | 121 |

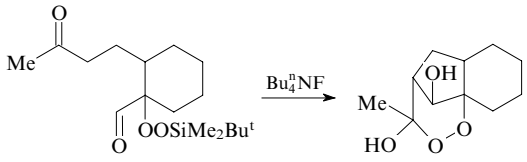
1,2,4-Trioxanes **143** structurally similar to the antimalarial drug artemisinin are obtained by intramolecular cyclization of triethylsilyl peroxides **144** catalyzed by TsOH in dichloromethane at room temperature.[128] The starting triethylsilyl peroxides **144** are synthesized in two stages. First, compounds **145** containing an exocyclic vinyl group are formed. Then, they are converted to silyl peroxides by the Isayama – Mukaiyama reaction (the yield of trioxanes **143** recalculated with respect to the corresponding compound **145** is given).[128]




**145** **144** **143**

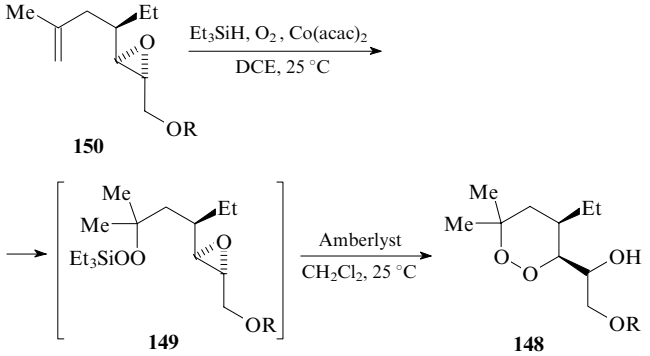
R = $Bu^n$ (28%), Ph (24%), Me (36%).

Intramolecular cyclization of 1-[*tert*-butyl(dimethyl)-silylperoxy]-2-(3-oxobutyl)cyclohexanecarbaldehyde (**146**) leads to the formation of 11-methyl-9,10-dioxatricyclo[6.3.1.$0^{3,8}$]dodecane-11,12-diol (**147**), which is also structurally similar to artemisinin.[185] The process is carried out under the action of tetrabutylammonium fluoride at room temperature.




**146** **147** (59%)

In the synthesis of 1,2-dioxanes **148,** the intermediates **149** are obtained by the Isayama – Mukaiyama reaction from alkenes **150**. In the final step, simultaneous removal of the triethylsilyl protecting group and cyclization is attained using the ion-exchange resin Amberlyst in the $H^+$-form.[42]



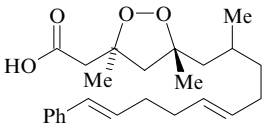

**150** **149** **148**

R = Ac (75%), $MeSO_2$ (45%).

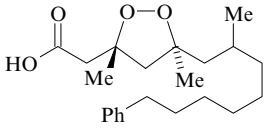
The 1,2-dioxane ring is contained in plakortin and dihydroplakortin, two natural endoperoxides exhibiting antimalarial activity.

Plakinic acids D (**151**) and E (**152**) are peroxides isolated from the sponge *Plakortis* sp.[186] They can be of interest as

substances that exhibit cytotoxic effect against tumour cells.[186] The pharmacophore group of these compounds is the 1,2-dioxolane ring.

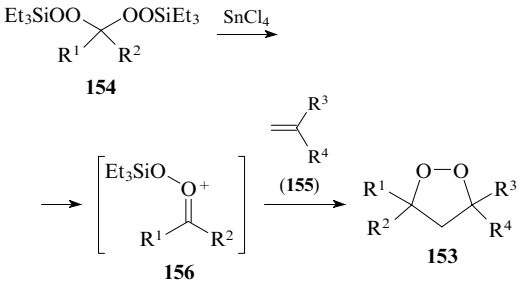


**151**



**152**

The synthesis of similar 1,2-dioxolanes **153** is based on the interaction of the bis(triethylsilyl) peroxides **154** with terminal alkenes **155** in the presence of tin tetrachloride.[88,187] The reaction proceeds *via* the formation of the peroxycarbenium ion **156**. The process is carried out in dichloromethane at −78 °C.



**154**

**156**

**153**

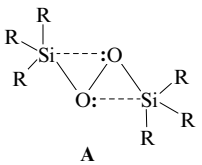
| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield (%) | Ref. |
|---|---|---|---|---|---|
| $Ph(CH_2)_2$ | Me | $BnO(CH_2)_2$ | Me | 57 | 88 |
| $(CH_2)_2CHMe(CH_2)_2$ | | $BnO(CH_2)_2$ | Me | 59 | 187 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | $BnO(CH_2)_2$ | Me | 80 | 88 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | $Me_3SiCH_2$ | H | 92 | 88 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | $HO(CH_2)_2$ | Me | 47 | 88 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | $EtO_2C(CH_2)_2$ | Me | 34 | 88 |
| $(CH_2)_2CHBu^t(CH_2)_2$ | | 4-$MeC_6H_4$ | H | 28 | 88 |

To conclude this Section, it should be noted that cyclic silicon-containing peroxides obtained by the reactions of organosilicon peroxides usually show high antimalarial[42,88,111,112,114,120–122,124,128,183–185,187] and cytostatic[186] activities. At present, these compounds are basic to the design of antiparasitic drugs.

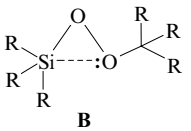
## VII. Rearrangements of organosilicon peroxides

A characteristic feature of organosilicon peroxides $R_3SiOOSiR_3$ and $R_3SiOOCR_3$ (R = Alk, Ar) is intramolecular coordination Si−O due to the interaction between vacant d-orbitals of the silicon atom and p-orbitals of the oxygen atom.[188,189]

This coordination favours higher thermal stability of the peroxides with SiOOSi and SiOOC units compared to dialkyl peroxides.[188–190]



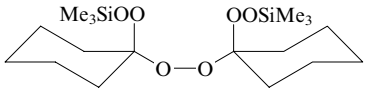
**A**



**B**

In addition, the **A**- or **B**-type coordination accounts for the ability of silyl peroxides to undergo rearrangements.[188,189,191–194]

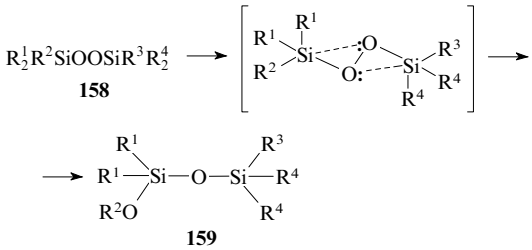
Taking thermolysis of 1,1′-bis(trimethylsilylperoxy)dicyclohexylperoxide (**157**) containing the COOC and SiOOC fragments as an example, it was shown that homolysis of the O−O bond in the COOC unit is the primary elementary step of the rearrangement.[190]



**157**

Dialkyl peroxides ROOR undergo homolytic decomposition to alkoxyl radicals RO when heated or under photolysis conditions.[20,21] The ability of organic peroxides to decompose to radicals with ease is widely used for initiation of radical processes.[195–205]

Unlike dialkyl peroxides, heating of organosilicon peroxides **158** mainly leads to intramolecular rearrangement with the formation of 1-alkoxy-1,1,3,3,3-pentaalkyl(aryl)disiloxanes **159** in high yields; the contribution of the homolytic decomposition channel is insignificant.



**158**

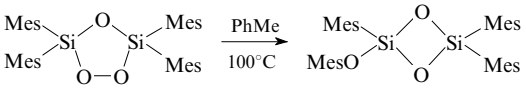
**159**

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield (%) | Ref. |
|---|---|---|---|---|---|
| Me | Me | Me | Me | – | 85 |
| Et | Et | Et | Et | – | 85 |
| $Pr^n$ | $Pr^n$ | $Pr^n$ | $Pr^n$ | – | 85 |
| Ph | Ph | Ph | Ph | 80–90 | 91 |
| | | | | 96 | 92 |
| Ph | Ph | Ph | Me | 80–90 | 91 |
| Ph | Ph | Me | Me | 80–90 | 91 |
| | | | | 99 | 195 |
| Ph | 4-$MeOC_6H_4$ | 4-$MeOC_6H_4$ | Ph | 70 | 92 |

Unlike dialkyl and disilyl peroxides, the decomposition of silyl peroxides $R^1R^2R^3SiOOCR^4R^5R^6$ on heating proceeds concurrently by the radical mechanism and through an intramolecular rearrangement.[206–209]

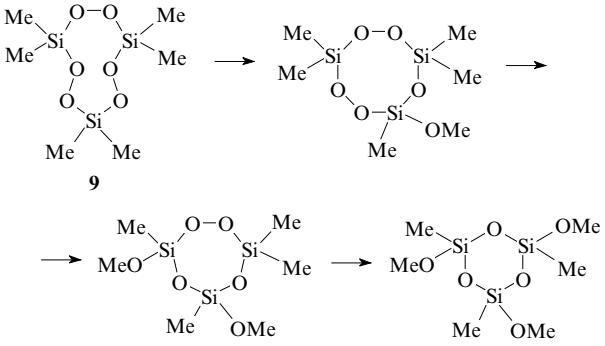
The stability of organosilicon peroxides depends on the nature of sustituents at the silicon atom. As a rule, alkylsilyl peroxides are more stable then arylsilyl peroxides.[85] The introduction of an electron-donating substituent into the phenyl moiety of arylsilyl peroxides reduces the stability of the compounds.[92,210] Organosilicon peroxides also become less stable as the number of peroxide groups at the silicon atom increases. In this case, the contribution of the homolytic decomposition channel increases compared to that of the heterolytic rearrangement.[211,212]

Cyclic organosilicon peroxides with the silicon atom in the ring are mainly rearranged to alkoxysilanes when heated. For example, 2,2,5,5-tetramesityl-1,3,4-trioxa-2,5-disilonane (**54a**) is transformed to 2,2,4-trimesityl-4-(mesityloxy)-1,3-dioxa-2,4-disiletane (**160**) in toluene at 100 °C in a yield of 94%.[74]



**54a** **160**

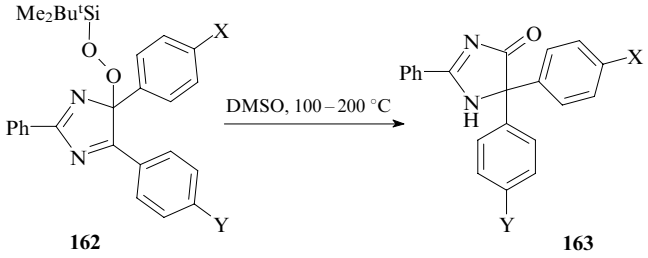
Heating of 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxa-3,6,9-trisilonane (**9**) causes the ring size to decrease and a methyl group to migrate from the silicon to the oxygen atom.[79]



**9** **161**

In the course of the reaction, reduction of the ring size from the nine-membered ring (**9**) to the six-membered one (perhydro-2,4,6-trimethyl-2,4,6-trimethoxy-1,3,5-trioxa-2,4,6-trisilyne, **161**) is accompanied by the change in the Si–O–Si bond angle. It approaches the values typical of cyclosiloxanes. Each subsequent step of the rearrangement proceeds slower than the preceding one.

Thermal rearrangement of imidazole silyl peroxides **162** to imidazolones **163** involves migration of the phenyl moiety and the formation of a carbonyl group.[213] The target imidazolones **163** are obtained in a yield of about 50%.



**162** **163**

X = H: Y = H, F; X = $CF_3$, Y = OMe.

It is believed that the rearrangement has an ionic nature. Dimethyl sulfoxide acts as a reducing agent and favours heterolytic dissociation of the O–O bond.

Summing up, organosilicon peroxides are mainly stable compounds. Their stabilities increase with an increase in the number of unperoxidized fragments in the molecule and with a decrease in the number of peroxide groups. Stable silicon peroxides are isolated in individual form by chromatography on silica gel. Usually, these compounds are characterised by $^1H$, $^{13}C$ and $^{29}Si$ NMR spectroscopies as well as by X-ray diffraction and elemental analysis.

## VIII. The synthesis and reactions of organogermanium peroxides

Organogermanium peroxides have been poorly studied so far.[3, 82, 83, 92, 214–220]

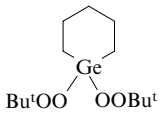
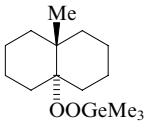
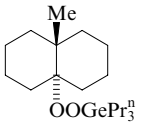
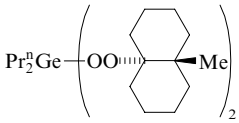
The main method of synthesis of organogermanium peroxides is the reaction of halogermanes with hydroperoxides **1** in the presence of nitrogenous bases (Table 8).

$$R^1_{4-n}GeX_n + R^2OOH \longrightarrow R^1_{4-n}Ge(OOR^2)_n + n\,HCl, \quad (4)$$

**1**

X = Cl, Br; $n$ = 1–4.

**Table 8**. Synthesis of organogermanium peroxides by reaction (4).

| Compound | Yield (%) | Ref. |
|---|---|---|
| $Pr^n_3GeOOBu^t$ | – | 3 |
|  | – | 3 |
|  | – | 3 |
|  | – | 3 |
|  | – | 3 |
| $Et_3GeOOBu^t$ | 80 | 82 |
| $Ph_3GeOOCPh_3$ | 54 | 82 |
| $Ph_3GeOOBu^t$ | 92 | 82 |
| $Ph_3GeOOCMe_2Ph$ | 78 | 82 |
| $Et_2Ge(OOBu^t)_2$ | – | 83 |
| $Ph_2Ge(OOBu^t)_2$ | – | 83 |
| $PhGe(OOBu^t)_3$ | – | 83 |
| $Ge(OOBu^t)_4$ | 70 | 83 |

Triethylamine [3] and ammonia [214] are used as bases. The reaction is carried out in diethyl ether [3, 214] or in pentane [3] on cooling. This method was used to obtain mono-, di-, tri- and tetrasubstituted organogermanium peroxides.[83]

Using hydrogen peroxide and chlorogermane **164**, one can obtain both hydroperoxygermanes **165a–c** and bis(triarylgermyl) peroxides **166a,b** depending on the $H_2O_2$ : **164** molar ratio.[92, 217–219]

$$\underset{\textbf{164a–c}}{R^1_2R^2GeCl} \xrightarrow[NH_3]{H_2O_2} \underset{\textbf{165a–c}}{R^1_2R^2GeOOH},$$

$R^1$ = Ph: $R^2$ = Ph (**a**, 60%), 4-$F_3CC_6H_4$ (**b**, 42%);
$R^1$ = $R^2$ = cyclo-$C_6H_{11}$ (**c**, 65%).

$$\underset{\textbf{164a,b}}{2\,RPh_2GeCl} \xrightarrow[NH_3]{H_2O_2} \underset{\textbf{166a,b}}{RPh_2GeOOGePh_2R},$$

R = Ph (**a**, 60%), 4-$F_3CC_6H_4$ (**b**, 57%).

The synthesis of peroxygermanes **165a**, **166a** from alkoxy- and aminogermanes was also reported.[82]

$$Ph_3GeOMe \xrightarrow{H_2O_2} Ph_3GeOOH + MeOH,$$
**165a**

$$2\,Ph_3GeNH_2 \xrightarrow{H_2O_2} Ph_3GeOOGePh_3 + 2\,NH_3.$$
**166a**

A method of synthesis of triethylgermyl hydrotrioxide ($Et_3GeOOOH$) based on ozonolysis of triethylgermane was proposed. The reaction is carried out in deuterated solvents at −78 °C. Raising the temperature to −60 °C causes triethylgermyl hydrotrioxide to decompose to singlet oxygen and triethylgermanol.[150]

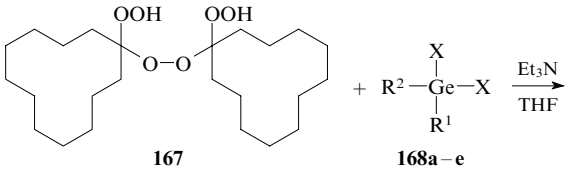
Most organogermanium peroxides synthesized are stable when heated to at most 70 °C. The thermal stability of compounds decreases as follows:[83]

$$Et{-}Ge(OOBu^t)_2{-}OOBu^t > Ph{-}Ge(OOBu^t)_2{-}OOBu^t > Ph{-}Ge(OOBu^t)_3 > Bu^tOO{-}Ge(OOBu^t)_2{-}OOBu^t.$$

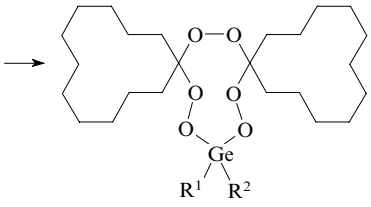
Reactions of 1,1′-dihydroperoxydi(cyclododecyl) peroxide (**167**) with disubstituted dihalogermanes **168** led to the first cyclic organogermanium peroxides, *viz*., 1,2,4,5,7,8-hexaoxa-3-germonanes **169** in yields from 31% to 59%.[220]

Attempts to synthesize 1,2,4,5,7,8-hexaoxa-3-germonanes by the reactions of low-molecular-mass 1,1′-dihydroperoxydi(cyclohexyl) peroxide and 1,1′-dihydroperoxydi(cycloheptyl) peroxide with dimethyl- and diethyldibromogermanes have failed. The germanium peroxides thus obtained decomposed during the synthesis.

Unlike the nine-membered silicon analogues, the germanium peroxides **169** rapidly decompose on storage and are hydrolyzed in air. Hydrolysis produces the starting 1,1′-dihydroperoxydi(cyclododecyl) peroxide **167** in a quantitative yield.



**167** **168a–e**



**169a–e**

| Compound **169** | $R^1$ | $R^2$ | X | Time /h | Yield (%) |
|---|---|---|---|---|---|
| **a** | Me | Me | Cl | 4 | 59 |
| **b** | Et | Et | Br | 7 | 43 |
| **c** | $Bu^n$ | $Bu^n$ | Br | 20 | 37 |
| **d** | Me | Ph | Br | 20 | 31 |
| **e** | Ph | Ph | Br | 20 | 41 |

* * *

In the present review, the main research publications concerning the methods of synthesis and reactions of organosilicon and organogermanium peroxides are generalized to the fullest extent. In spite of some advances, a general problem in chemistry of these compounds is low selectivity of their synthesis. Restrictions on the nature of functional groups for carrying out the peroxidation reactions should also be mentioned. In addition, the potential of these peroxides as oxidizng agents and reactants for the introduction of silyloxy groups has not been realized as yet.

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