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Gerald L. Larson, Editor
VP, Research Products
Gelest, Inc.
11 East Steel Road
Morrisville, PA 19067

ORGANOSILYL PEROXIDES

A. Ricci, G. C. Seconi, R. Curci, and
G. L. Larson

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1. INTRODUCTION

The chemistry of organic peroxides has been studied for many years, due in large part to their diverse and useful chemistry. The entrance of the silyl peroxides brings into this area another class of peroxides that shows, in general, greater stability and greater selectivity of reaction than many of the carbon-based peroxides. The further development of the chemistry of the silyl peroxides will depend to a large degree on the ability to produce them at commercially viable scales and economics. It is hoped that this chapter will stimulate further study of the silyl peroxides and their synthesis.

2. PREPARATIVE METHODS

2.1. Silylhydroperoxides

Silylhydroperoxides, though relatively unstable, can be readily prepared either by treating 95% hydrogen peroxide with a silylamine or with a chlorosilane in the presence of a base as a hydrogen chloride acceptor (eqs. 1 and 2).[1] The thermal stability of the silylhydroperoxides is increased with increasing steric bulk of the silyl group: triphenylsilylhydroperoxide with a melting point of 110–112 °C is, for example, indefinitely stable at room temperature.

$$R_3SiNH_2 + H_2O_2 \xrightarrow{Et_2O} R_3SiOOH \qquad (1)$$

$$R_3Si = Ph_3Si;\ MePh_2Si;\ (PhCH_2)_3Si;\ (^nC_6H_{13})_3Si$$

$$Me_3SiCl + H_2O_2 \xrightarrow{C_5H_5N} Me_3SiOOH + C_5H_5NHCl \qquad (2)$$

2.2. Silylalkylperoxides and Silylarylperoxides

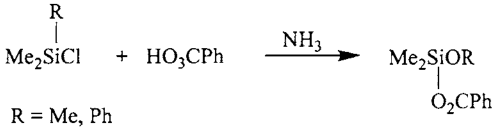
Alkyl- and arylperoxysilanes are the most thermally stable of the peroxysilanes and, in turn, the most extensively studied derivatives of peroxysilanes.[2a] They are most conveniently prepared by nucleophilic substitution of a chlorosilane by the corresponding alkyl- or arylhydroperoxide in the presence of an HCl acceptor (eq. 3).[2b] This general reaction has been used to prepare a wide range of alkylperoxysilanes in generally good yields. Alternatively, the reaction of the sodium salt of the hydroperoxide with a chlorosilane or an alkylhydroperoxide with a silylamine can be used to prepare this class of peroxysilanes.

$$\mathrm{R^1_{4\text{-}n}SiCl_n} + n\,\mathrm{R^2OOH} \xrightarrow{\text{Base}} \mathrm{R^1_{4\text{-}n}Si(OOR^2)_n} + n\,\text{Base-HCl} \qquad (3)$$

Base = pyridine, triethylamine, ammonia

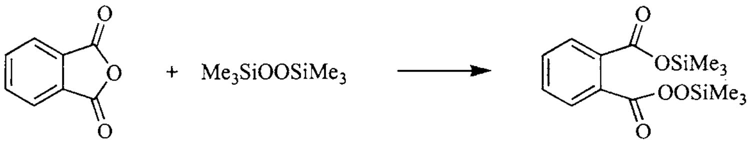
2.3. Silylperoxy Esters

In spite of the numerous efforts to prepare peroxybenzoyltrimethylsilane from the reaction of trimethylchlorosilane and peroxybenzoic acid, the isolation of the target compound has been thus far unsuccessful due to a facile migration of a methyl group from silicon to carbon with concomitant migration of the benzoate group to silicon to form the methoxybenzoyloxydimethylsilane (eq. 4)[2b] The reaction of bis(trimethylsilyl)peroxides with phthalic anhydride has been shown to give the peroxyester (eq. 5). It is unclear why there is no facile rearrangement in this preparation.[2c]



$$\overset{\mathrm{R}}{\overset{|}{\mathrm{Me_2SiCl}}} + \mathrm{HO_3CPh} \xrightarrow{\mathrm{NH_3}} \underset{\mathrm{O_2CPh}}{\underset{|}{\mathrm{Me_2SiOR}}} \qquad (4)$$

R = Me, Ph



(5)

2.4. Bis(silyl)peroxides

The peroxy moiety in bis(silyl)peroxides can be generated directly from hydrogen peroxide and a suitable silylating agent and many synthetic routes have been developed following this general concept. Thus, for example, bis(triphenylsilyl)peroxide has been prepared from the reaction of 98% hydrogen peroxide and triphenylchlorosilane in 53% yield with ammonia as an HCl acceptor (eq. 6).[1] Alternatively, this product can be prepared by the reaction of hydrogen peroxide and triphenylsilylamine (eq. 7).[1]

$$2\ Ph_3SiCl + H_2O_2 \xrightarrow{NH_3} Ph_3SiOOSiPh_3 \tag{6}$$

$$2\ Ph_3SiNH_2 + H_2O_2 \longrightarrow Ph_3SiOOSiPh_3 \tag{7}$$

The use of disodium peroxide as the peroxide source has been proposed[3] (eq. 8). The reported compound obtained from the reaction of disodium peroxide with trimethylchlorosilane was only about 80–85% pure, but was suitable for many uses without distillation.

$$Na_2O_2 + 2\ Me_3SiCl \longrightarrow Me_3SiOOSiMe_3 + 2\ NaCl \tag{8}$$

Attempts to employ oxygen and ozone in the preparation of peroxysilanes was successful with the reaction of oxygen and bis(trimethylsilyl)diimine[4] (eq. 9), but not with the treatment of tetraethylsilane with ozone, which leads to triethylsilanol and hexaethyldisiloxane instead of the peroxysilane (eq. 10)[5].

$$R_3Si\text{-}N{=}N\text{-}SiR_3 + O_2 \longrightarrow R_3SiOOSiR_3 + N_2 \tag{9}$$

$$\begin{array}{l} Et_4Si + O_3 \ \not\longrightarrow \ Et_3SiOOSiEt_3 \\ \quad \llcorner\!\longrightarrow Et_3SiOH + Et_3SiOSiEt_3 \end{array} \tag{10}$$

Bis(triphenylsilyl)peroxide can also be obtained by the reaction of triphenylsilylhydroperoxide with triphenylchlorosilane in the presence of a tertiary amine[1] (eq. 11), a procedure which can be used for the preparation of unsymmetrical bis(silyl)peroxides.

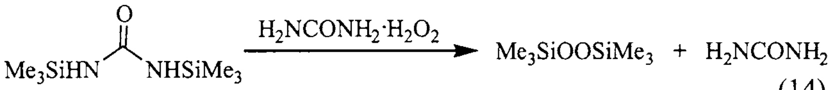
$$Ph_3SiOOH + Ph_3SiCl \xrightarrow{Et_3N} Ph_3SiOOSiPh_3 \tag{11}$$

Triphenylgermylperoxide was shown to react with triphenylsilylamine to give triphenylsilyl(triphenylgermyl)peroxide (eq. 12).[6]

$$Ph_3GeOOH + Ph_3SiNH_2 \longrightarrow Ph_3GeOOSiPh_3 + NH_3 \tag{12}$$

All the practical procedures that allow bis(trimethylsilyl)peroxide to be conveniently produced start from a stabile preformed hydrogen peroxide-base complex,[7] which is reacted with an appropriate silylating agent. According to this general strategy the synthesis of the bis(silyl)peroxides was proposed and carried out by Davies[8] leading to good yields with a relatively simple procedure. More recently a modified version of this approach was shown to be more convenient.[9,10] Even more recently it was shown that the commercially available urea or hexamethylene tetramine hydrogen peroxide complex can be reacted with bis(trimethylsilyl)urea to give bis(trimethylsilyl)peroxide and urea.[11] The product is readily separated from the insoluble urea by-product (eqs. 13 and 14).

$$4\ Me_3SiCl + N(CH_2CH_2)_3N \xrightarrow[CH_2Cl_2/0\ °C]{DABCO/H_2O_2} 2\ Me_3SiOOSiMe_3 + 2\ N(CH_2CH_2)_3NHCl \qquad (13)$$



(14)

All of the above-mentioned preparations appear suitable for the preparation of relatively large samples of bis(trimethylsilyl)peroxide as well as other desired bis(silyl)peroxides.

2.5. Bis(trimethylsilyl)Caro's Acid

The reaction of bis(trimethylsilyl)peroxide with sulfur trioxide in dichloromethane provides bis(trimethylsilyl)caro's acid, a common reagent for Baeyer–Villiger reactions (eq. 15).[12]

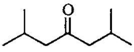
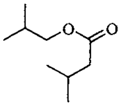
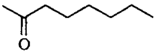
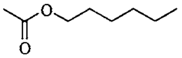
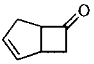
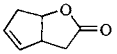
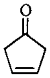
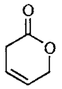
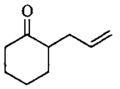
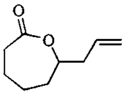
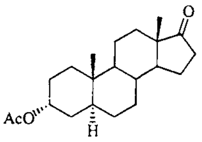
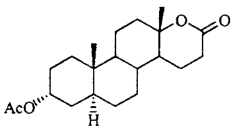
$$Me_3SiOOSiMe_3 + SO_3 \xrightarrow[-30\ °C]{CH_2Cl_2} Me_3SiOSO_2OOSiMe_3 \qquad (15)$$

3. BAEYER–VILLIGER AND RELATED OXIDATIONS

3.1. Baeyer–Villiger Oxidation of Ketones

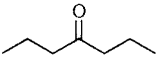
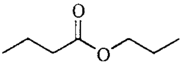
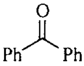
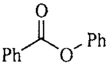
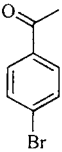
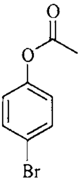
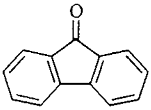
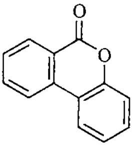
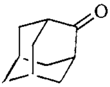
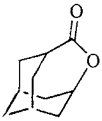
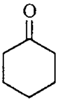
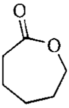
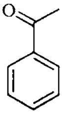
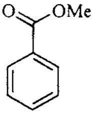
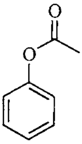
Bis(trimethylsilyl)peroxide (BTMSPO) in the presence of a catalytic amount of trimethylsilyl triflate is useful for the Baeyer–Villiger oxidation of ketones (eq. 16).[13] The oxidation occurs exclusively at the carbonyl functionality leaving olefins unreacted. Thus, when an equimo-

Table 1. Baeyer–Villiger Oxidation of Ketones with $Me_3SiOOSiMe_3$ According to Equation 16

Entry	*Substrate*	*Product*	*Yield (%)*
1			40
2			24
3			75
4			42
5			40
6			85

carbonyl functionality leaving olefins unreacted. Thus, when an equimolar mixture of cyclohexanone and cyclohexene was treated with BTMSPO only 6-hexanolide and cyclohexene were observed with no detection of cyclohexene oxide. Table 1 shows examples of the Baeyer–Villiger oxidation of ketones with BTMSPO in the presence of trimethylsilyl triflate. Bicyclo[3.2.0]hept-2-en-6-one lead exclusively to a key prostaglandin intermediate (entry 3). The oxidation of 3-cyclopentenone afforded solely 3-penten-5-olide (entry 4). This lies in sharp contrast to the oxidation by trifluoroperacetic acid, which produces only 3,4-epoxycyclopentanone. The reaction of 1-allylcyclohexanone takes place in a

Table 2. Baeyer–Villiger Oxidation of Ketones with Bis(trimethylsilyl)monoperoxysulfate

Entry	*Ketone*	*Product Ester*	*Yield %*
1			96
2			83
3			98
4			74
5			88
6			94
7		 	benzoate 20% acetate 80%

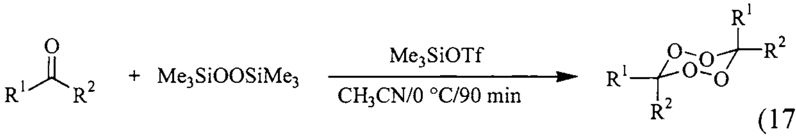
Oxidation of the 17-keto group of steroids is possible[14] (entry 6). Aromatic ketones are not employable with the attempted oxidation of arylalkyl ketones resulting in complex reaction mixtures.

$$R^1R^2C{=}O \; + \; Me_3SiOOSiMe_3 \xrightarrow{Me_3SiOTf} R^1CO_2R^2 \; + \; Me_3SiOSiMe_3 \qquad (16)$$

The Baeyer–Villiger oxidation with BTMSPO can also be performed with the assistance of tin tetrachloride or boron fluoride etherate as catalysts with results comparable to those employing trimethylsilyl triflate as the catalyst.[15]

Bis(trimethylsilyl)monoperoxysulfate exhibits promise as a Baeyer–Villiger oxidant.[16] Dioxiranes have been suggested as the reactive intermediates in the mechanism of oxidation in these reactions. Some of the limitations of this reagent are the sluggish reaction of α,β-unsaturated ketones, the oxidation of double bonds, and that arylalkyl ketones are converted to phenols. Some of the Baeyer–Villiger oxidations with bis(trimethylsilyl)monoperoxysulfate are given in Table 2.

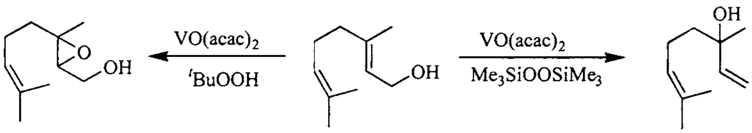
Under specific conditions the reaction of ketones with BTMSPO can be shifted from the formation of esters or lactones to 1,2,4,5-tetroxanes, a class of compounds with potential antimalarial properties (eq. 17).[17]



(17)

R^1,R^2 = –(CH$_2$)$_5$–; –CH$_2$CMe$_2$CH$_2$CMe$_2$CH$_2$–; –(CH$_2$)$_2$O(CH$_2$)$_2$– Me, Me; H, Ph; H, ^{n}C$_5$H$_{11}$; H, ^{n}C$_9$H$_{19}$

The VO(acac)$_2$ or Mo(acac)$_2$ catalyst activated with BTMSPO effectively induces the isomerization of allylic alcohols in contrast to the well-known Sharpless epoxidation of such systems (eq. 18).[18]



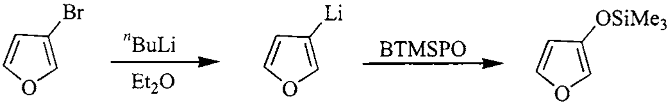
(18)

3.2. Reaction with Carbanions

Under the very mild conditions of less than 100 °C and aprotic solvents, BTMSPO undergoes reaction with various reagents that do not react with, for example, di-*tert*-butylperoxide. The reaction of BTMSPO with organolithium reagents is shown in Table 3 (eq. 19). In these reactions the BTMSPO acts as a source of electrophilic oxygen resulting in the controlled oxidation of the lithium reagent, a conversion that is particularly useful in the synthesis of phenols.[9] As shown by the examples in Table 3, this method of synthesizing phenols provides high regioselectivity, which is often lost in standard procedures. The method appears to be especially useful for the generation of *ortho*-substituted phenols due to the ready generation of a number of *ortho*-substituted aryllithium reagents.

$$\begin{array}{ccc} \text{R-Li} + \text{Me}_3\text{SiOOSiMe}_3 & \longrightarrow & \text{R-OSiMe}_3 + \text{LiOSiMe}_3 \\ & & \Big\downarrow \text{H}_2\text{O} \\ & & \text{R-OH} + 1/2\ \text{Me}_3\text{SiOSiMe}_3 \end{array} \qquad (19)$$

The preparation of 3-trimethylsiloxyfuran was accomplished as shown below. This material was used as a Diels–Alder diene in the reaction with maleic anhydride (eqs. 20 and 21).[19]



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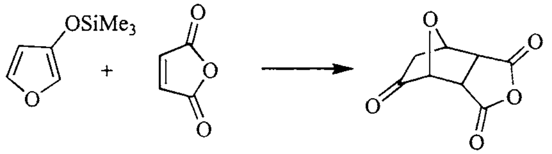
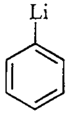
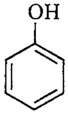
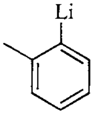
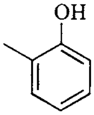
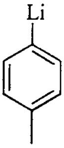
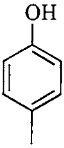
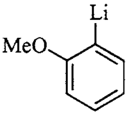
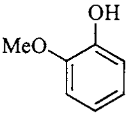
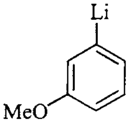
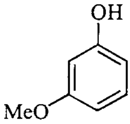
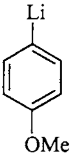
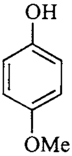
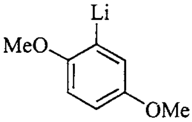
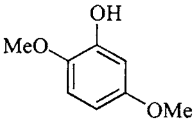
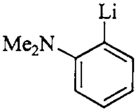
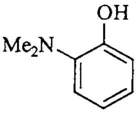
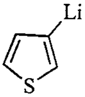
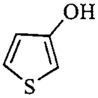


(21)

The extension of this methodology to a wider range of carbanionic systems demonstrates the potential of BTMSPO as a readily handled oxidizing agent, with the potential oxidations seemingly being limited to the formation of the desired carbanion.[20] These oxidations are shown schematically in Scheme 1. The reaction of enolates provides the α-hydroxy carbonyl system as the result of reaction at the carbon center, except for the direct reaction at silicon which provides the trimethylsilyl enol ether. As can be seen, both of the two possible reaction pathways

Table 3. Oxidation of Organolithium Reagents with $Me_3SiOOSiMe_3$ According to Equation 19

Entry	*Lithium Reagent*	*Product*	*Yield %*
1			86
2			83
3			51
4			68
5			88
6			61
7			40
8			43
9			65

(continued)

Table 3. (Continued)

Entry	*Lithium Reagent*	*Product*	*Yield %*
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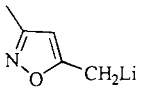
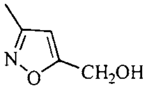
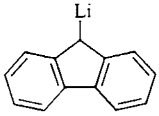
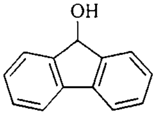
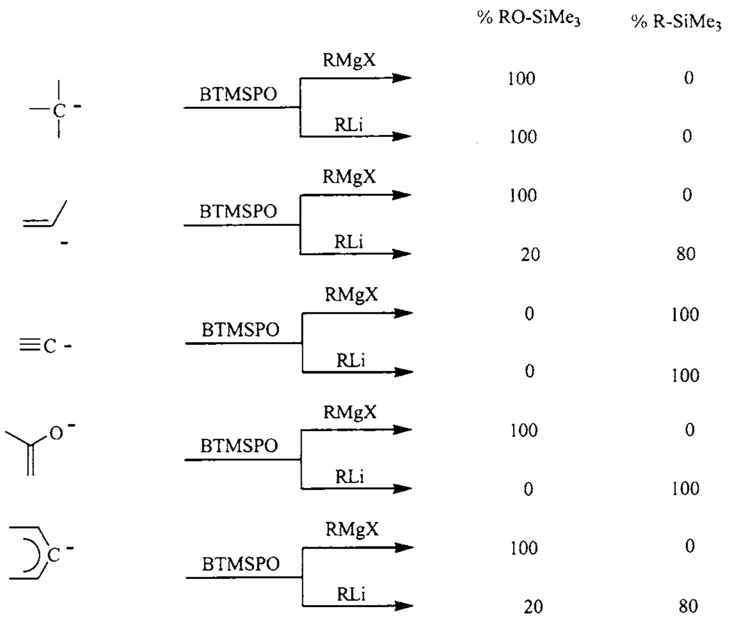
11			39
12			75

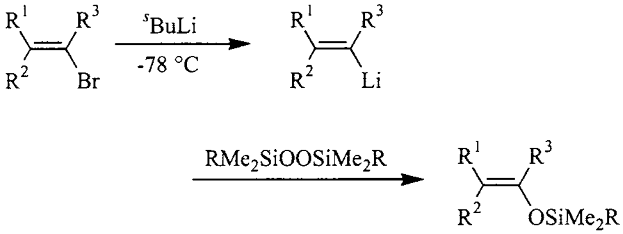
occur, namely reaction at the electrophilic oxygen and reaction of the carbanion at the silyl group. Alkyl systems and aryl- and vinylmagnesium halides react exclusively at oxygen, while vinyl-, aryl-, and ethynyllithium reagents react preferentially at silicon. Halomagnesium enolates react at oxygen with their lithium counterparts reacting at silicon. The



Scheme 1.

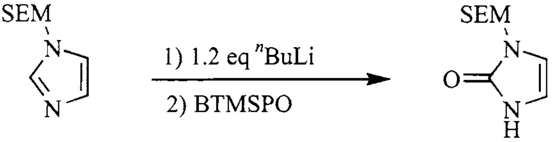
relative rates of the two pathways can be changed for vinyl- and aryllithium reagents upon changing the method for preparing the carbanions.[20] Among the organometallic reagents, Grignard reagents give the best results in the oxysilylation process with the efficacy of the reaction being in the order of: alkyl > aryl > heteroaryl > vinyl > heterosubstituted alkyl = alkynyl. Aspects of the mechanism are discussed in Section 7. A general rule of guidance can be the HSAB rule where one considers the silyl atom as a hard acid and the oxygen as the softer acid.

Advantage can be taken of the conversion of vinyl bromides to vinyl lithium reagents[21] and then to enol silyl ethers with retention of regio- and stereochemistry as shown in eq. 22.



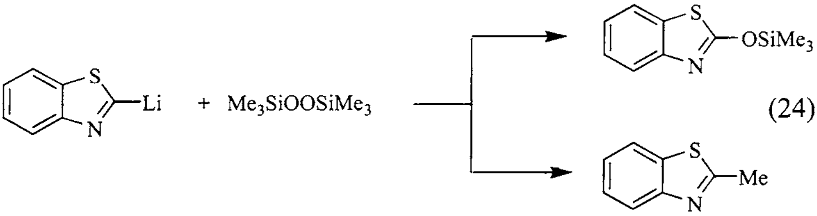
(22)

The lithium reagents of N-SEM protected imidazoles can be quenched with BTMSPO leading directly to imidazolones (eq. 23).[22]



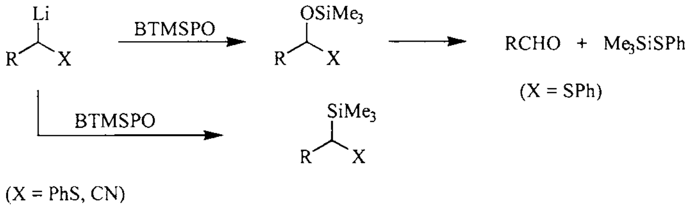
(23)

An unprecedented and puzzling demethylation of BTMSPO by certain carbon nucleophiles has been reported. It would seem that in the reaction of lithiated alkylbenzothiazoles with BTMSPO, the formation of methylated products competes with the formation of silyl ethers (eq. 24).[23]



(24)

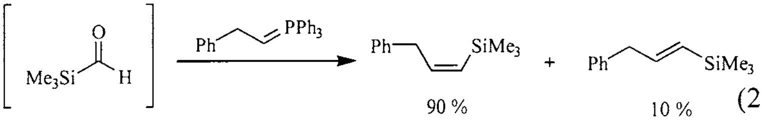
The reaction of BTMSPO with lithium derivatives of sulfides and nitriles has been reported to give the corresponding *O*-trimethylsilyl hemithioacetals and cyanohydrins, respectively.[24] From these products the carbonyl function can be exposed in acidic media or in the presence of fluoride ion. This methodology provides an attactive route to the conversion of a sulfide or nitrile to an aldehyde. As an example, the highly unstable trimethylsilylformaldehyde was prepared in situ by the route shown in eqs. 25–29. Similar reactions were reported for alkyl, allyl, benzyl, and cycloalkyl sulfones as well.[25]



(25)

(26)

(27)



(28)

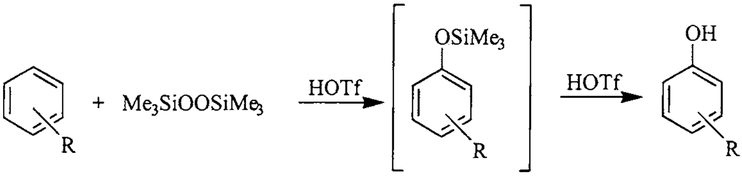
$$R^1R^2CHLi + Me_3SiOOSiMe_3 \longrightarrow R^1R^2CO + Me_3SiOSiMe_3 \qquad (29)$$

3.3. Electrophilic Hydroxylation of Aromatics

Electrophilic hydroxylation of *o*- and *p*-xylene using a range of peroxides, including BTMSPO, in the presence of Lewis acids has been reported. Mixtures of phenols, involving those by ipso attack followed by rearrangement are obtained and important differences are evident from a comparison of the BTMSPO-based results with those obtained using Fenton's reagent.[26] More recently the BTMSPO/triflic acid combination has been described as a highly effective hydroxylating agent for aromatics (eq. 30).[27] This method is safer and more effective than those previously developed. Some results are given in Table 4.

Table 4. Oxidation of Aromatics with $Me_3SiOOSiMe_3/HOTf$

			Isomer Distribution		
Substrate	*T (°C)*	*Yield %*	*ortho*	*meta*	*para*
Benzene	0	77			
Toluene	0	88	63	10	27
Mesitylene	–50	94			
o-Xylene	–50	63	48(2,3–)	22(2,6–)	30(3,4–)
Naphthalene	0	92	67(a–)		33(b–)
Chlorobenzene	0	76	63		37



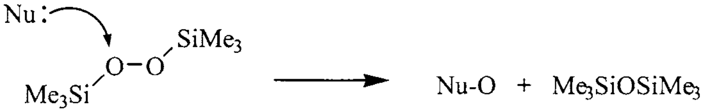
(30)

4. REACTIVITY AND SYNTHETIC APPLICATIONS

The reactivities and applications of the silyl peroxides can be a function of their structures. The bis(trimethylsilyl)peroxide is the most studied of the peroxysilanes. The most obvious application of the peroxysilanes is as an oxidant for heteroatoms such as sulfur, nitrogen, and phosphorus. This section deals with such heteroatom oxidations.

4.1. Oxidation of Sulfur, Nitrogen, and Phosphorus

It has been pointed out that bis(trimethylsilyl)peroxide and *tert*-butyl-(trimethylsilyl)peroxide might be considered as analogs to hydrogen peroxide in the oxidation of sulfides to sulfoxides and sulfones.[28,29] (eqs. 31–35) Both of these silyl peroxides give similar rates in the oxidation of 1-thia-4-oxacyclohexane,[30] which are higher than those observed for the oxidation with *tert*-butylhydroperoxide or di-*tert*-butylperoxide, which are nearly unreactive under the same conditions as those employed with the silyl peroxides. The oxidation of tertiary amines to N-oxides occurs, but is some 700 times slower than the oxidation of thiols.[30] The conversion of phosphites to phosphates[28b] can also be accomplished under mild conditions and the BTMSPO has been used for the generation of the P=O bond and the transformation of the P=S and P=Se bonds to P=O bonds.[31]



(31)

$$Me_3\,SiOOSiMe_3 + Me_2S \rightarrow Me_2SO + Me_3SiOSiMe_3 \quad (32)$$

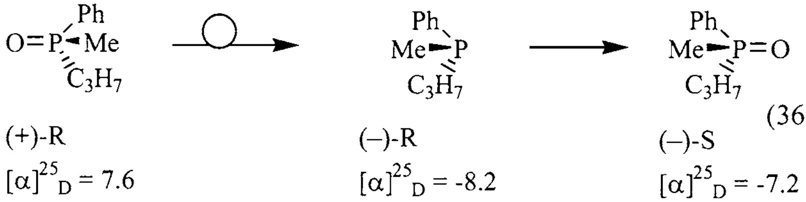
$$Me_3\,SiOOSiMe_3 + Me_2SO \rightarrow Me_2SO_2 + Me_3SiOSiMe_3 \quad (33)$$

$$Me_3\,SiOOSiMe_3 + (EtO)_3P \rightarrow (EtO)_3PO + Me_3SiOSiMe_3 \quad (34)$$

$$Me_3\,SiOOSiMe_3 + EPh_3 \rightarrow OEPh_3 + Me_3SiOSiMe_3 \quad (35)$$

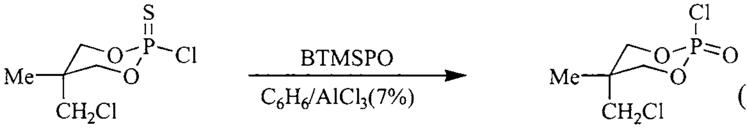
$$(E = P, As, Sb)$$

High yields and high stereoselectivities of the oxidations with silyl peroxides make them particularly suitable for synthetic applications. Thus, for example, in those cases which exclude the possibility of employing protonated oxidizing agents or where the gaseous reagents such as oxygen, ozone, and nitrogen oxides lead to by-products, the use of BTMSPO can be a distinct advantage. This is especially true in the oxidation of phosphines, which occurs with retention of configuration at phosphorus (eq. 36).[32]



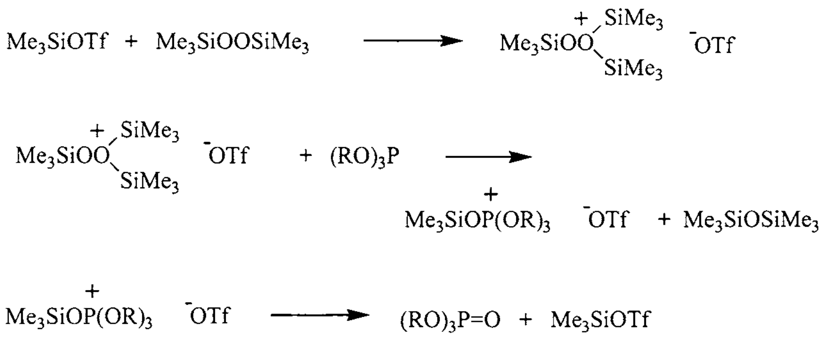
(36)

Whereas oxyphosphoryl derivatives are obtained with retention of configuration at the phosphorus atom (eq. 37), conversion of the thiophosphoryl function to the oxyphosphoryl group occurs with inversion of configuration at phosphorus.[32]



(37)

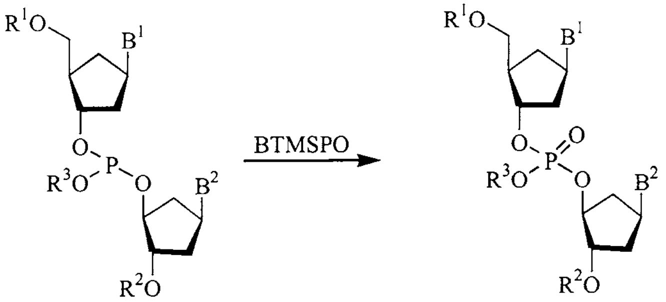
Considerable attention has been paid to the oxidation of organophosphorus compounds in connection with the rapid development of the chemistry of bioactive phosphorus-containing products (Scheme 2, eqs.



Scheme 2.

38 and 39). For example, the BTMSPO oxidation of phosphites to phosphates in nucleosides and nucleopeptides is accomplished under nonaqeous conditions and can be done in the solid phase.[33] This represents significant advantages over the conventional aqueous iodine oxidation, which requires drying steps. The oxidation is facilitated by the addition of a catalytic amount of trimethylsilyl triflate or its resin-supported version, Nafion-TMS.[34] The silyl triflate may act as a simple acid catalyst without breaking the Si–O bond.

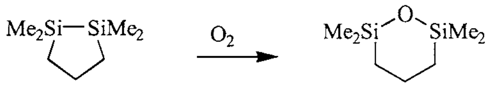
$$(PhO)Me_2Si(CH_2)_nPPh_2 \xrightarrow[n = 2,3]{BTMSPO} (PhO)Me_2Si(CH_2)_nP(O)Ph_2 \quad (38)$$



(39)

4.2. Cleavage of the Silicon–Silicon Bond

BTMSPO acts as an oxygen transfer agent to the Si–Si bond.[35] A possible mechanism could involve the electrophilic attack of oxygen on the Si–Si bond wherein the silylperoxide acts as an "oxenoid" O-insertion reagent (eq. 40).



(40)

5. UMPOLUNG TRANSFER OF HALIDES AND PSEUDOHALIDES WITH BTMSPO

The observation that alkynyl anions react with BTMSPO in the presence of zinc iodide gives rise to terminal iodoalkynes, made available a ready synthesis of 1-iodoalkynes (eq. 41). This procedure offers major advantages over existing methods in terms of fewer by-products and the ability to tolerate other functional groups, and has led to the synthesis of 1-halo(psuedohalo)alkynes in general.[36] Some results are given in Table 5.

$$\mathrm{R{-}C{\equiv}C{-}H} \; + \; \mathrm{MXn} \; \xrightarrow[\mathrm{THF}]{\mathrm{BTMSPO}} \; \mathrm{R{-}C{\equiv}C{-}X} \qquad (41)$$

M = Cu, Zn; n = 1,2
X = Cl, Br, I, CN

Table 5. Functionalized 1-Alkynes from BTMSPO and MX_n in THF According to Equation 41

Entry	*R*	*MX_n*	*R–C≡C–X*	*Yield (%)*[a]	*$(R{-}C{\equiv}C)_2$ Yield (%)*
1	Ph	ZnI_2	Ph–C≡C–I	90(85)[b]	10
2	$^nC_3H_7$	ZnI_2	n-C_3H_7–C≡C–I	45	—
3	Ph	CuI	Ph–C≡C–I	80	15
4	$^nC_3H_7$	CuI	n-C_3H_7–C≡C–I	40	2
5	Me_3Si	CuI	Me_3Si–C≡C–I	90(80)[b]	—
6	$^nC_8H_{17}$	CuI	n-C_8C_{17}–C≡C–Br	70	—
7	Ph	CuCl	Ph–C≡C–Cl	50	40
8	Ph	CuBr	Ph–C≡C–Br	75(70)	25
9	$^nC_8H_{17}$	CuBr	n-C_8H_{17}–C≡C–Br	80	—
10	Me_3Si	CuBr	Me_3Si–C≡C–Br	70(60)[b]	—
11	$(Me_3Si_2)NHCH_2$	CuBr	$(Me_3Si)_2NCH_2$–C≡C–Br	45	—
12	Ph	CuCN	Ph–C≡C–CN	70(65)[b,c]	30

Notes: [a] Yields are based on alkynes and were determined by GC.
[b] Isolated yields.
[c] 2.2 equivalents of CuCN were used.

6. CARBON OXIDATION IN NEUTRAL SYSTEMS

BTMSPO is a suitable cooxidant able to convert alcohols to carbonyls in the presence of chromium (VI) or ruthenium (II) complexes as catalysts in dichloromethane.[37,38] The BTMSPO–pyridinium dichromate system has proved to be effective for the generation of the oxodiperoxinium complex (**1**), a key reagent for the oxidation of alcohols. Some results are given in Table 6.

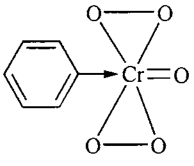


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Table 6. Oxidation of Alcohols with Pyridinium Dichromate (**1**)/$Me_3SiOOSiMe_3$

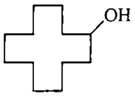
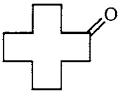
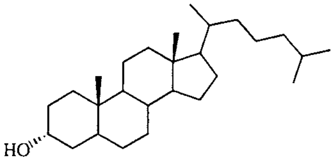
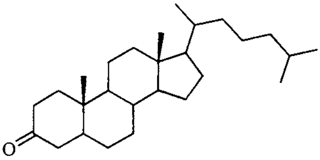
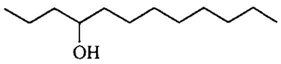
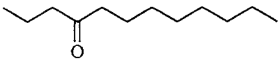
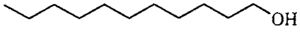
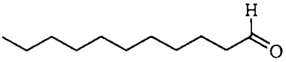
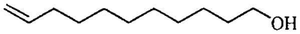
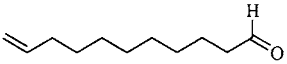
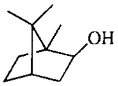
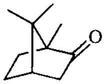
Entry	*Substrate*	*Product*
1		
2		
3		
4		
5		
6		

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Table 6. (Continued)

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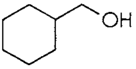
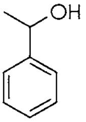
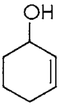
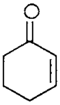
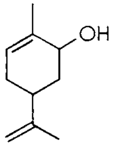
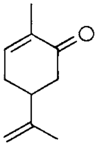
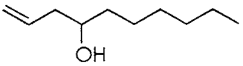
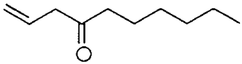
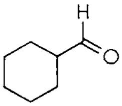
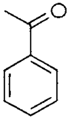
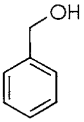
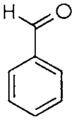
7		
8		
9		
10		
11		
12		

The coexisting olefinic linkages remain intact upon treatment with the above complex and no epoxy compounds were observed. The combination of BTMSPO with a ruthenium complex, $RuCl_2(PPh_3)_3$, shows that simple mixing of the substrate, the catalyst, and the oxidant is again highly effective in the oxidation of alcohols as shown in Table 7. Worthy of special note is the oxidation of allyl alcohols with configurational retention of the double bond. As expected, primary alcohols are oxidized faster than secondary alcohols with the $RuCl_2(PPh_3)_3$–BTMPO system with the relative rates being from 20–40:1. This fact can be utilized in the selective oxidation of a primary alcohol in the presence of a secondary one. These results are given in Table 8.

Table 7. Oxidation of Alcohols with $RuCl_2(PPh_3)_3/Me_3SiOOSiMe_3$

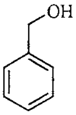
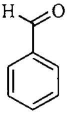
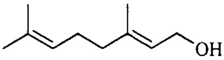
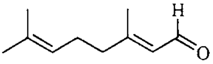
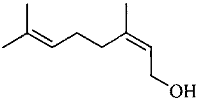
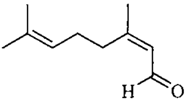
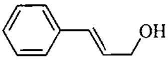
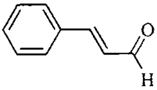
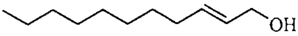
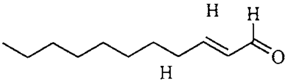
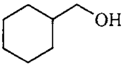
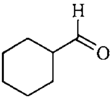
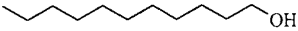
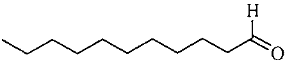
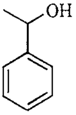
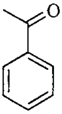
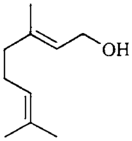
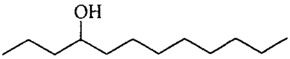
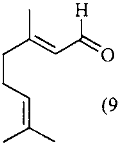
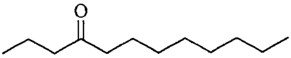
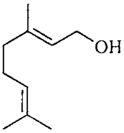
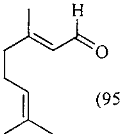
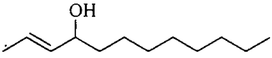
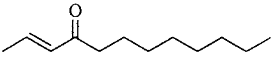
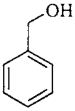
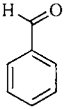
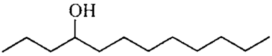
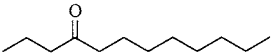
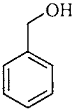
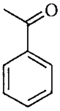
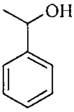
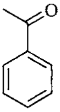
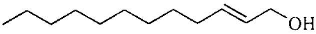
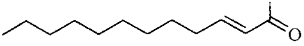
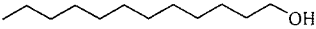
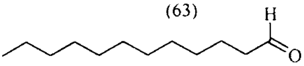
Entry	*Substrate*	*Product*
1		
2		
3		
4		
5		
6		
7		
8		

Table 8. Selective Oxidation of Primary Alcohols in the Presence of Secondary Alcohols

Entry	*Alcohol Mixture*	*Products (% Yields)*
1	 	 (99)  (3)

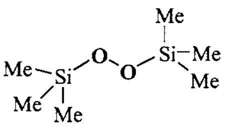
(continued)

Table 8. (Continued)

Entry	*Alcohol Mixture*	*Products (% Yields)*
		 (95)
2		 (6)
3		 (98)
		 (8)
4		 (85)
		 (6)
5		 (63)
		 (40)

7. REACTION MECHANISMS OF ORGANOSILICON PEROXIDES

Although the potential of organosilicon peroxides has been well developed in organic synthesis during the last few decades, their reaction mechanisms appear to have been little explored. By and large, the reactivity guidelines and mechanisms that are well established for analogous non-silicon organic peroxides have been adopted in order to envisage reaction pathways of organosilicon peroxides.[39] The rationale behind



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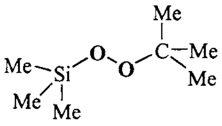
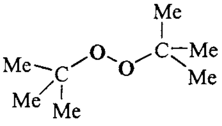


3



4

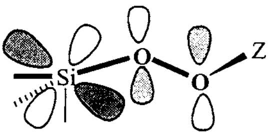
this lies in the structural analogies existing between organosilicon peroxides and their carbon counterparts, as shown by structures **2**, **3**, and **4**.

Indeed, it can be reasonably expected that—akin to common organic and inorganic peroxides[40]—reaction mechanisms involving silyl peroxides will be largely dominated by the weakness of the peroxide O–O bond ($D°_{298}$ from 50 to 25 kcal mol^{-1}), which is prone to either homolytic or heterolytic cleavage. By comparison, in organic compounds normally Si–O and Si–C bond strengths range from 90 to 110 and 70 to 80 kcal mol^{-1}, respectively.[39]

Once granted this major feature is common, it is also recognized that organosilicon peroxides should have some peculiarities of their own which may come into play. For instance, in inspecting **2**, **3**, and **4**, the Me_3Si– group only superficially resembles a *t*-butyl group; in fact, the steric shielding of the O–O bond by the trimethylsilyl group is considerably less than the Me_3C– due to the fact that the Si–O bond is significantly longer than the C–O bond (i. e., ca. 1.63 vs. 1.47 Å). In **2** the Si–O bond length measured 1.68 Å[41] and ranks among the longer Si–O bonds recorded.

More important, the Me_3Si– group (the "organic proton") is easily transferred to a variety of oxygen-containing functional groups so that in certain reactions the reactivity of **2** and **3** could be expected to more closely resemble that of their protic peroxide analogs, i.e. HOOH and *t*-BuOOH.

Other relevant features derive from the fact that silicon atoms—due to the empty *d*-orbitals—should be particularly effective in delocalizing electrons pertaining to the adjacent O–O bond through d_π–p_π-interactions with the filled π^*-orbitals of the peroxide group, as in **5**.



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In a review of this length, the range and depth of topics must be limited, thus an exhaustive coverage of the literature is not feasible. Therefore, we shall restrict ourselves to sketching the relevant principles that rule silylperoxide reactivity by presenting a limited number of pertinent examples.

7.1. Thermolysis and Photolysis

The amount of energy required to carry out the homolytic cleavage[40,42] of a generic peroxide, ZOOY, varies from 47 kcal mol^{-1} for HOOH down to values such as 23 kcal mol^{-1} for phenylacetylperoxide $[PhCH_2C(:O)O]_2$, which undergoes multiple bond cleavage.[43] In the latter, contributing to the ease of homolytic bond scission, is an entropy of activation of about +12 cal $mol^{-1}K^{-1}$.

The kinetics of the thermal decomposition of some simple silyl peroxides has been studied.[44–47] Some experimental values of $\Delta H^{\neq}$ and of $\Delta S^{\neq}$ for peroxide bond homolysis are given in Table 9.

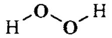
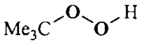
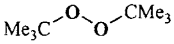
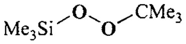
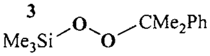
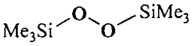
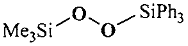
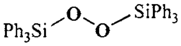
Data in Table 1 reveal that *t*-butyl trimethylsilyl peroxide (**3**) is remarkably stable toward thermolysis with temperatures of 180–200 °C being necessary to achieve measurable decomposition rates.[44,45] This is 60–70 °C higher than is required for its carbon analog di-*t*-butyl peroxide (**4**), as reflected in an activation enthalpy of 41 vs. 36 kcal mol^{-1}. On going from **3** to cumyl trimethylsilyl peroxide (**6**), by introducing a phenyl group in place of methyl in the alkyl moiety this situation does not change. Therefore, it seems that simple trialkylsilyl alkyl peroxides[44,45] are remarkably more stable than their analogous dialkyl peroxides. This might be ascribed to the mentioned silicon–oxygen d_π–p_π-bonding, which should relieve repulsive lone-pair interactions between the two adjacent peroxide oxygens; thus, the O–O bond would be less prone to homolytic cleavage.

Akin to di-*t*-butyl peroxide, for the thermolysis of **3** and **6** a homolytic mechanism is signaled by a positive activation entropy. Also, the main reaction products observed,[44,45] i.e. Me_3SiOH and $Me_2C{=}O$ (or Ph–CO–Me) are easily rationalized on basis of formation of $Me_3SiO^\bullet$ and *t*-$BuO^\bullet$ (or $Me_2PhC{-}O^\bullet$) radicals. Formation of $(Me_3Si)_2O$, another major prod-

$$Me_3SiO^\bullet + Me_3Si{-}O{-}O{-}{}^tBu \longrightarrow Me_3Si{-}O{-}SiMe_3 + {}^\bullet O{-}O{-}{}^tBu \qquad (44)$$

$${}^tBuOO^\bullet \xrightarrow{-(1/2)\,O_2} {}^tBuO^\bullet + Me_2C{=}O + Me^\bullet \qquad (45)$$

Table 9. Activation Parameters for Some Simple Silyl Peroxides and Related Species

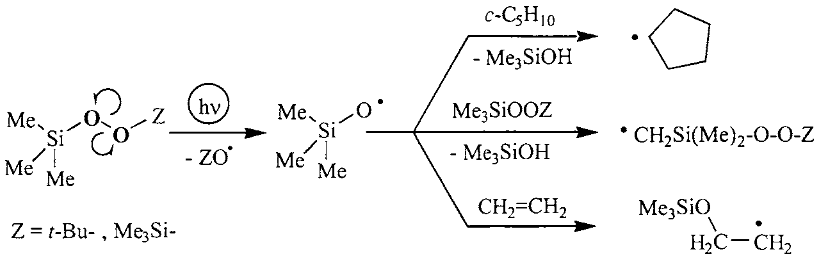
Peroxide	$\Delta H^{\neq}$ *(kcal mol^{-1})*	$\Delta S^{\neq}$ *(cal mol^{-1}K^{-1})*
	47	$+11^{a}$
	41	$+12^{a}$
 **4**	36	$+14^{a}$
 **3**	41	$+11^{b,c}$
 **6**	41	$+11.5^{d,e}$
 **2**	32	$-0.8^{b,h}$
 **7**	28	-4^{a}
 **8**	47	$-4^{f,h}$

Notes: [a]Most data are from ref. 41.
[b]*n*-Heptane solvent.
[c]Calculated from data reported by Hiatt (ref. 44).
[d]*n*-Nonane solvent.
[e]Calculated from data reported by Yablokov et al. (ref. 45).
[f]Anisole solvent.
[g]Ref. 47.
[h]Ref. 46.

uct, can be accommodated envisaging the occurrence of an S_H2 type process at silicon by trimethylsiloxyl radicals (eqs. 44 and 45).

In photolysis experiments,[48,49] *t*-butyl trimethylsilyl peroxide (**3**) and bis(trimethylsilyl)peroxide (**2**) show in common a behavior which can be attributed to the formation of trimethylsiloxyl radical (Scheme 3).

During photolysis of **2** and **3** over a temperature range from −120 to −20 °C, ESR monitoring revealed the presence of radicals resulting from reactions (1) in cyclopentane solvent, (2) in cyclopropane, which is

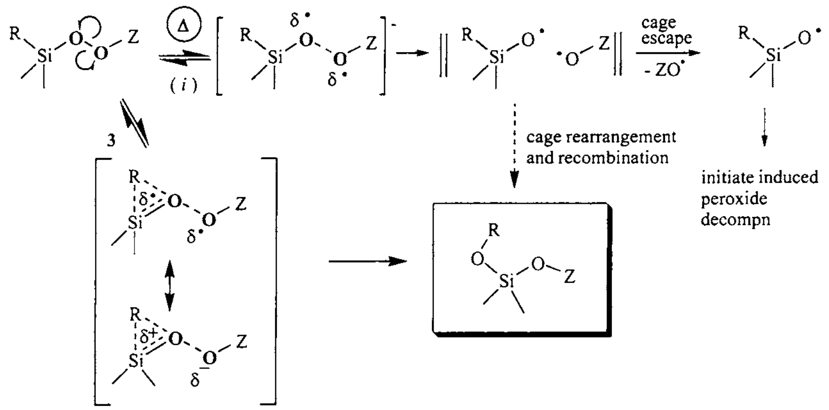


Scheme 3.

resistant to H-abstraction, or (3) in the presence of ethylene.[49] The latter reaction, consisting of the addition of the trimethylsiloxyl radical to ethylene, is quite telling; in fact, it has been known for some time that simple silyl peroxides can initiate the free-radical polymerization of alkenes either thermally or photochemically.[50]

Returning to thermolysis, inspection of data in Table 9 reveals that the decomposition of bis(silyl)peroxides (last four entries) is remarkably easier than their silyl, alkyl, or dialkyl analogs. In fact, the rates of thermal decomposition can be conveniently measured in the range 150–170 °C for bis(trimethylsilyl)peroxide (**2**),[46] from 120 to 140 °C for other bis(trialkylsilyl)peroxides,[49] and from 80 to 100 °C for bis(triphenylsilyl)peroxide (**8**).[47] In fact, on going from **3** to **2**, the activation enthalpy drops by some 9 kcal mol^{-1}! Also, in the series of the bis(silyl)peroxides, substitution of methyl with phenyl groups (which has a superior migratory attitude), brings down the $\Delta H^{\neq}$ value by about 4–5 kcal mol^{-1} (cf. Table 9). Also, the activation entropy values become negative, and just one major reaction product is formed, i.e. $RO–SiR_2–OSiR_3$ derived from the rearrangement of the peroxide $R_3SiOOSiR_3$.[6,46,48] All these facts point to the occurrence of an assisted, somewhat concerted process of O–O bond cleavage, such as the one sketched in Scheme 4 (path *ii*). Given certain favorable structural features, path *ii* may become a viable reaction channel alternative to simple homolysis (path *i*, Scheme 4).

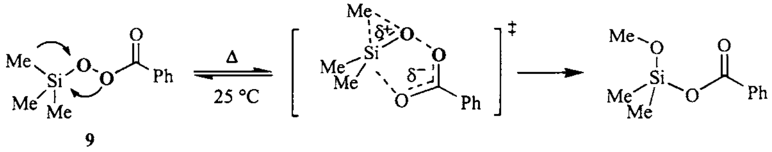
Along path *ii* in Scheme 4 above, one should notice that the radical transition state (hereafter t.s.) could have some ionic (polar) contribution in leading to the rearrangement product. An alkyl or aryl group would then migrate more or less concertedly with O–O bond cleavage in order to mitigate the energetically unfavored charge separation. In fact, for a series of substituted bis(silyl)peroxides p-XC_6H_4–$Si(Ph)_2$–OO–



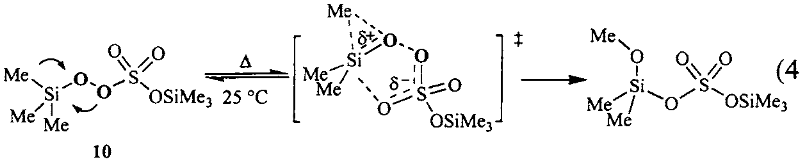
Scheme 4.

Si(Ph)$_2$C$_6$H$_4$X-*p* the relative migratory aptitudes of the aryl groups have been found to be X = *p*-MeO (6.0) > *p*-CH$_3$ (1.1) > H (1.0).[6] These effects are relatively small, however, arguing for only *partial* ionic contribution to the description of a transition state whose prevailing nature is radical.

It is likely that the ionic contribution to the transition state for decomposition is much greater for silyl peroxides derived from organic or inorganic peroxyacids. For instance, trimethylsilyl peroxybenzoate (**9**) and bis(trimethylsilyl)peroxymonosulfate (**10**) rearrange quite rapidly *even at room temperature* into their non-peroxide isomers (eqs. 46 and 47).[2a]



(46)



(47)

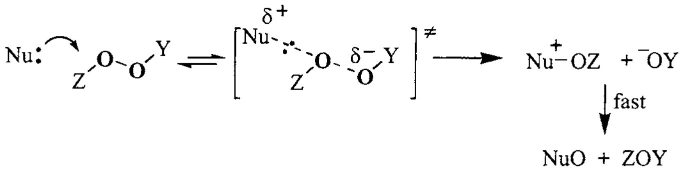
This speaks for a low-barrier to multiple-bond cleavage in the transition state, facilitated by the greater stability of the incipient benzoate (or sulfate) anion with respect to simple alkoxide RO^-. The absence of products coming from diffusion of radicals out of the solvent cage argues against the incursion of radical-induced decomposition, and several facts indicate that a simple O–O bond homolysis process does not take place. For instance, the carbon analog of **9**, i.e. *t*-butyl peroxybenzoate PhC(:O)OOBu-*t*, undergoes thermolysis at 100–120 °C with $\Delta H^{\neq} = 34$ kcal mol^{-1} and $\Delta S^{\neq} = 10$ cal $mol^{-1}K^{-1}$,[51] meaning a rate constant of the order of 10^{-10} s^{-1} at 25 °C; this points to a decomposition which is much slower than that of **9**. The enhanced rate recorded for **9** can not be solely due to the greater stability of $Me_3SiO^{\bullet}$ with respect to *t*-$BuO^{\bullet}$, as can be seen by estimating the rate of decomposition of a simple process of O–O homolysis, i.e. **9** Æ $PhC(:O)O^{\bullet} + {}^{\bullet}OSiMe_3$. The estimate can be carried out in the following way.

The data in Table 9 can be used to estimate $\Delta H^{\neq}$ for homolysis of other peroxide species, and hence rate constants at various temperatures, provided one makes the reasonable assumption that $\Delta H^{\neq}$ for a mixed peroxide ZOOY is the mean of the activation enthalpies of ZOOZ and YOOY. For the process at hand, we employ the enthalpy values of 32 and 29 kcal mol^{-1} for $Me_3SiOOSiMe_3$ (Table 9) and benzoyl peroxide PhC(:O)–OO–C(:O)Ph,[52] respectively; the mean of these two values is 30.5 kcal mol^{-1}. Using this for $\Delta H^{\neq}$, and the value of +5 cal $mol^{-1}K^{-1}$ for $\Delta S^{\neq}$, the rate constant for simple O–O homolysis of **9** at 25 °C is estimated to be ca. 5×10^{-9} s^{-1}! This is clearly several powers of 10 higher than the rate of decomposition of silyl peroxyester **9**.

The very low rate estimated suggests that simple (i.e., noncatalyzed) homolysis of silyl peroxyesters in solution is usually overwhelmed by low-energy multiple-bond cleavage processes such as those sketched above (eqs. 46 and 47). However, careful kinetic studies are needed in order to verify this notion.

7.2. Electrophilic Oxidation

Selective oxidation of organic substrates by peroxyacids, hydroperoxides,[40,53a–c] and other reactive peroxides[53d] is one of the most important transformations in organic synthesis; it is widely employed to achieve selective, non-radical O-transfers either in noncatalytic or catalytic[40,53,54] processes. In many instances, the most plausible mechanism involves nucleophilic attack by the substrate at the weak O–O bond of the peroxide; in fact, the usual heterolytic reaction of a generic peroxide ZOOY is bimolecular with another species (a nucleophile, Nu:) bringing up a pair of electrons to that oxygen which is losing its grip on the O–O bonding electrons (eq. 48).[40]



(48)

In terms of frontier molecular orbitals (FMO),[55] the HOMO of the nucleophile interacts with the first LUMO of the peroxide, i.e. the s^* of the O–O moiety, to form a new bond. This is shown in Figure 1 for the case of hydrogen peroxide, the simplest peroxide species.

As can be noted in Figure 1, this process is similar in several ways (e.g. the stereoelectronic requirement for linearity of Nu:--O--O in the transition state) to nucleophilic attack at carbon in methyl halide. In fact, a number of kinetic studies[40] have provided evidence in support of a close parallelism between nucleophilic attack at the peroxide O–O bond and at sp^3 carbon. From these it is possible to describe the characteristics of electrophilic oxidation by peroxides, i.e. nucleophilic displacement on the peroxide O–O bond, as follows:

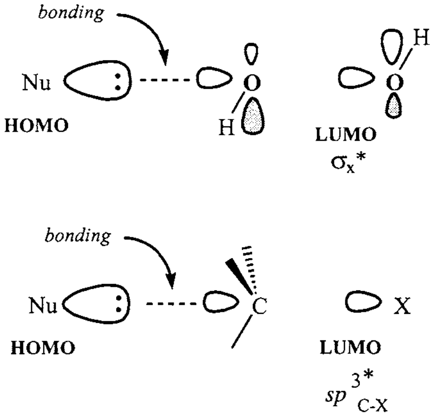


Figure 1. Frontier molecular orbitals for nucleophilic displacement at the O–O bond and at sp^3 carbon.

(1) The most reactive nucleophiles are strongly polarizable (e.g. I^-, Br^-,R_2S, R_3P), whereas the most basic ones (e.g. HO^-) are rather unreactive, and alkenes are very poorly reactive.

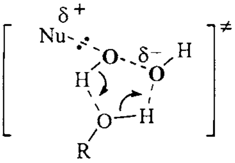
(2) The direction of electron motion in the transition state (cf. eq. 48) is favored when the leaving anion ^-OY is less basic (i.e. when Y is more electron-withdrawing), which makes ^-OH a poor leaving group; hence H_2O_2 is less reactive with respect to peroxyacids (leaving group RCO_2^-). In general, for protic peroxides YOOH the reactivity markedly depends on the nature of Y, and there is a good correlation of log k with the pK_a of YOH (i.e. the conjugate acid of leaving group YO^-); as these become weaker bases, they are also better leaving groups, and rates increase.

(3) The characteristic rate law is first-order each in peroxide and the substrate (second-order overall), i.e. v = k_2[peroxide][Nu]; when, as in the case of H_2O_2 and alkyl hydroperoxides, the peroxide is poorly reactive, a third-order term is often found with acid (or other protic species) HA as added concentration, i.e., v = k_2[peroxide][Nu] + k_3[peroxide][Nu][HA].

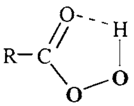
Acid catalysis aside, a hydroxylic solvent, for example alcohols, can also participate[40,56] as a component molecule in a cyclic transition state to transfer a proton to the leaving group, for instance as shown in transition state **11**.

The advantage gained by this solvent participation finds itself in the fact that endothermic charge separation (cf. eq. 48) is largely avoided. For organic sulfides oxidation by H_2O_2, the order of rates in hydroxylic solvents has been found to be related to the solvent autoprotolysis constants pK_{ROH}, e.g. AcOH > H_2O > MeOH > t-BuOH, with the range covering nearly four powers of 10.[56]

The concept of decreased charge separation in the transition state bears also on the oxidation of nucleophiles by peroxycarboxylic acids, but the mode differs. If the peroxyacid is present in a nonpolar, nonbasic solvent (e.g. benzene, CCl_4, $CHCl_3$, etc.), it exists in the ground state as



11



12

an internally *H*-bonded cyclic form (**12**);[53] this can react directly with the substrate, moving the proton to the carbonyl oxygen while the nucleophile is attacking the outer oxygen. Thus, charge separation in the transition state is again maximized.

Having recalled the principles which govern O-transfers by standard peroxides, it is of interest here to compare the features that earmark the electrophilic reactivity of silyl peroxides.

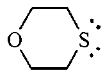
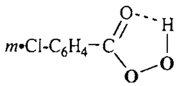
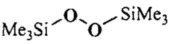
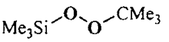
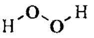
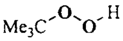
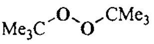
As it is seen by the synthetic applications reviewed in the previous sections, bis(trimethylsilyl)peroxide (**2**) can be considered analogous to hydrogen peroxide in that it readily oxidizes nucleophilic organic substrates as, for example, sulfides to sulfoxides, sulfoxides to sulfones, phosphines to phosphine oxides, phosphites to phosphates among others; also *t*-butyl trimethylsilyl peroxide (**3**) easily oxidizes phosphines to phosphine oxides.[2a] In these cases, one could envisage the same general mechanism of nucleophilic displacement at the O–O bond outlined in eq. 48 (with Z = Me_3Si–, and Y = Me_3Si– or *t*-Bu). Also, reaction stoichiometries are uncomplicated, simply reflecting O-transfer from the silyl peroxide to yield the oxidized substrate (NuO, in eq. 48).

Some kinetic data is available[30] which allow a comparison of the reactivity of simple silyl peroxides with that of standard peroxide oxidants toward model[56] organosulfur and nitrogen nucleophiles. These are collected in Table 10.

From data in Table 10, it is seen that oxidation of thioxane by bis(trimethylsilyl)peroxide (**2**) occurs over 30 times faster than the alkylamine, triethylamine, and over 700 times faster than the arylamine *N,N*-dimethyl *p*-anisidine (entry 2); this is also the trend of decreasing nucleophilicity of the substrates toward the peroxide O–O bond.[40,53] With reference to a single substrate (i.e. thioxane), the reactivity of the silyl peroxides lies in between that of peroxyacids and that of hydrogen peroxide or hydroperoxides. There can be no doubt that the trend is largely determined by the leaving group effect mentioned above; in fact the leaving group basicity varies by approximately 19 powers of 10 on passing from the peroxyacid (leaving group RCO_2–), to bis(trimethylsilyl)peroxide (**2**) (leaving group Me_3SiO^-), to di-*t*-butyl peroxide (leaving group *t*-BuO^-); in parallel the rates decrease by a factor 10^{10} (Table 10).

One must notice that the rates of silyl peroxides **2** and **3** become practically the same if one divides the rate of **2** by a statistical factor of 2; their reactivity exceeds that of *t*-BuOOH by a factor of almost 10^2 and that of *t*-BuOOBu-*t* by over 10^4. It was advanced[30] that a rationale behind

Table 10. Relative Rates of Oxidation of Thioxane and of Tertiary Amines by Silyl Peroxides as Compared to Related Peroxide Species at 25.0 °C[a,b]

Peroxide[c] *YOOZ*	pK_aYOH[d]		Et_3N	$Ar\text{-}\ddot{N}Me_2$[e]
	4.0	$> 5 \times 105$[f]	5×10^2[f]	3.5×10^2[f]
	10.0	1.0	3×10^{-2}	1.4×10^{-3}
	—[g]	0.6	—	—
	15.7	2.5×10^{-2}	—	—
	~ 19.	0.8×10^{-2}	—	—
	~ 19.	$< 0.5 \times 10^{-4}$	—	—

Notes: [a] Most data from ref. 30, or unpublished by Curci et al.

[b] In chloroform.

[c] With respect to thioxane oxidation by $Me_3SiOOSiMe_3$, k2g – $2.5 \times 10^{-2} M^{-1} s^{-1}$.

[d] Acidity constant of conjugate acid of leaving group YO^-.

[e] Ar = *p*-MeOC6H$_4$.

[f] Roughly estimated from data at lower temperatures.

[g] For this compound, due to nucleophilic attack at the oxygen attached to the Me_3Si– group, formally the leaving group is *t*-BuO$^-$ ($pK_a^{t\text{-BuOH}} \sim 19$); however, the displacement is likely to be assisted by a concerted 1,2-shift of the trimethylsilyl group (see text).

the enhanced reactivity can be found in the ability of the Me_3Si– group to assist O–O bond cleavage during nucleophilic attack, giving rise to bridged transition state structures[57] such as that in Figure 2.

In fact, the simple rate law (clean second order, order one each in substrate and in silyl peroxide), and the solvent effect observed speak for a bridged transition state, wherein a Me_3Si– group 1,2-shift concerted with O–O breaking serves to minimize charge separation (see above). This hypothesis is also supported by recent theoretical calculations at the MP4/6-31G*//MP2/6-31G* level performed on bis(silyl)peroxide H_3Si–

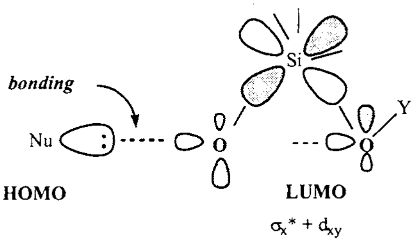


Figure 2.

OO–SiH_3;[58] these show that a bridging silyl group helps to stabilize the departing H_3SiO^- anion, and it is considerably more efficient in dispersing the developing negative charge than a proton.[59]

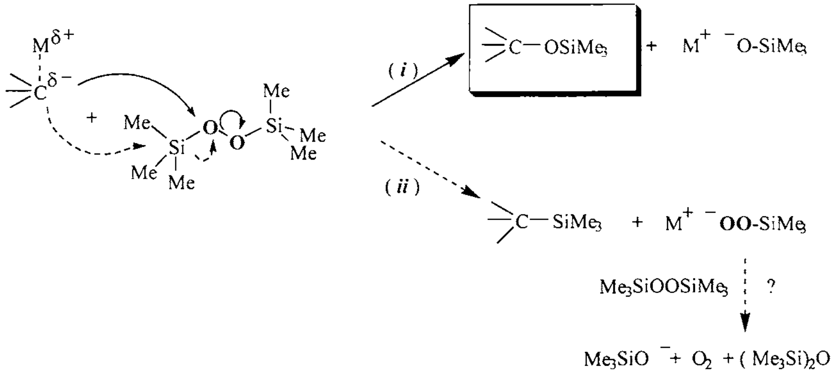
It is clear that the same pattern of O-transfer set forth in eq. 44 (i.e. nucleophilic attack at the peroxide O–O bond) can be envisaged for the oxidation of negatively charged nucleophiles, including carbanions. The latter, however, constitute a special case since—as it was shown in Section 3.2—in some instances the products show that oxysilylation (Me_3SiO^- group transfer) is accompanied by silylation (R_3Si– group transfer).[20] The latter process is even prevalent with the less basic alkynyl and other carbanions[20,22] (cf. Section 5). Clearly, besides nucleophilic attack at the O–O bond, another channel, namely attack at silicon, should be available to carbanions, as represented in Scheme 4 for attack at bis(trimethylsilyl)peroxide (**2**).

In Scheme 4, path *ii* represents S_N2-type attack at silicon, which is facilitated by the fact that Me_3SiOO^- (akin to HOO^-)[40,53a] should be a good leaving group.

None of the patterns outlined in Scheme 4 can substantiate the claim by Florio et al.[23] that **2** is capable of Me group transfer to carbanions, thus feigning common alkylating agents; hence, this exotic finding is still open to question since not even its overall reaction stoichiometry appears to have been defined.

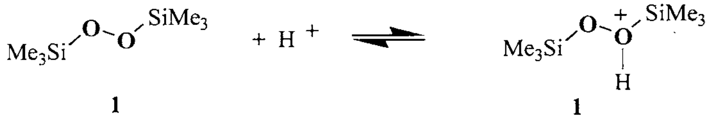
Concerning the reactivity of organometallics in general, one should be aware that their interaction with silyl peroxides (similar to H_2O_2 and other peroxides) might trigger one-electron radical processes;[40] thus, in order to unravel mechanisms, detailed kinetic and product studies are needed when changing the substrate nature or reaction conditions.

On the ground of a parallel with hydrogen peroxide,[40] one can bring out the way by which electrophilic oxidations using silyl peroxides can be activated by strong acids. In fact, addition of a strong acid to the level

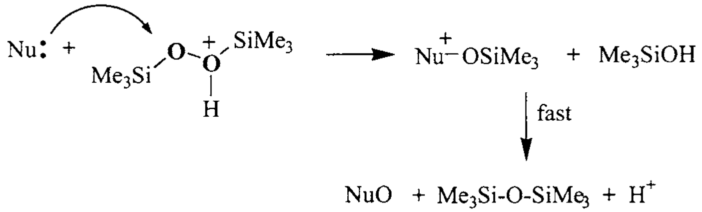


Scheme 4.

of 1 M H^+ often raises the rate of oxidation of nucleophiles by H_2O_2 by about two powers of 10.[40] It has been shown that this occurs by specific acid catalysis involving two steps, the first representing equilibrium protonation of the peroxide. A similar process might apply to simple silyl peroxides such as bis(trimethylsilyl)peroxide (**2**) (eqs. 49 and 50). Here, the rate increases because the leaving group is now the weak base Me_3SiOH rather than the strong base Me_3SiO^-.



(49)



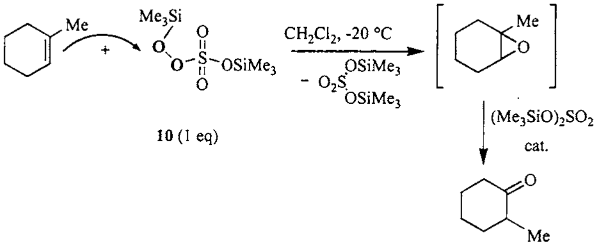
(50)

Using strong acids (e.g. triflic acid CF_3SO_2OH = TfOH), a sizable fraction of the silyl peroxide is expected to be protonated, giving the more electrophilic peroxonium ion **2′** (eq. 47); thus oxysilylation of *p*-donor systems, such as aromatic hydrocarbons, becomes feasible (cf. Section 3.3).

Parallel to this, in view of the mentioned ease of transfer of the Me_3Si–group to oxygenated functional groups, it is perhaps not surprising that the silyl derivatives of strong acids (e.g. Me_3SiOTf) in organic solvents should act as catalysts in oxidations by **2**. In fact, equilibrium formation of $Me_3Si–O–O^+(SiMe_3)_2$ species would provide a better leaving group than its parent peroxide, i.e. $(Me_3Si)_2O$ vs. Me_3SiO^-, and therefore enhanced capability of O-transfer to nucleophilic substrates.

Concerning strong acid catalysis in oxidations, one should be warned that this might also bring about undesirable acid-catalyzed rearrangement of the silyl peroxide; this is particularly true for those species whose silyl groups carry substituents prone to 1,2-migration (see above).

It has been shown[16b] that bis(trimethylsilyl)peroxymonosulfate (**10**) at –20 °C—in competition with decomposition (see above)—is capable of olefin oxygenation; this proceeds through formation of an epoxide, followed by rearrangement to a ketone (cf. eq. 51).



10 (1 eq)

(51)

The higher O-transfer power of **10** with respect to simple silyl peroxides such as **2** should be ascribed to enhanced leaving group ability, i.e. $(Me_3SiO)_2SO_2$ vs. $(Me_3Si)_2O$. In the epoxide to ketone rearrangement (cf. eq. 50), **2** or rather its reduction product $(Me_3SiO)_2SO_2$ could act as an "acid-equivalent" catalyst in the same way as Me_3SiOTf does (see above).

7.3. Nucleophilic Oxidation

At first glance it might seem contradictory that a silyl peroxide, which is an electrophilic oxidant, can be a reactive nucleophile (an electron-pair donor) at the same time. However, this can be seen to be possible in analogy to protic peroxide species ZOOH, e.g. hydrogen peroxide, hydroperoxides ROOH, or peroxyacids RC(:O)OOH. For instance, nucleophilic attack by ZOOH at an unsaturated moiety such as a carbonyl C=O, as catalyzed by acids or bases,[40] leads to intermediate adducts that might have sufficient kinetic stability to be detected spectroscopically,[60] or even be isolated. In most cases, however, the adducts would rather break down to products in a rapid subsequent step with O–O bond cleavage. An appropriate example is the well-known Baeyer–Villiger reaction,[61] allowing the transformation of ketones into esters.

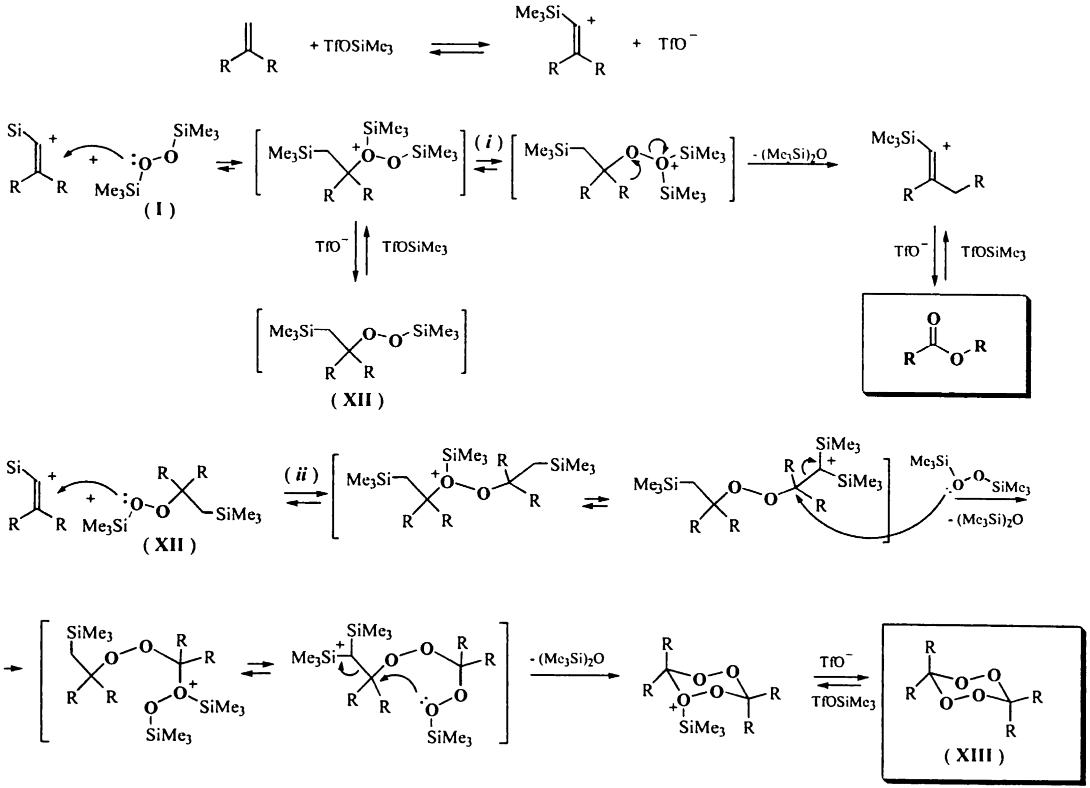
On these grounds, it is perhaps not surprising that bis(trimethylsilyl)peroxide (**2**) has been found to be a suitable agent for the transformation of a variety of ketones into esters when using trimethylsilyl trifluoromethanesulfonate $TfOSiMe_3$ as catalyst (see Section 5).[13] In the sequence outlined in Scheme 5, the key step involves the formation of the α-(silyloxy)alkyl silylperoxide (**13**), which then undergoes rapid trimethylsilyl triflate-catalyzed rearrangement into ester (path *i*).

As in the generation of α-hydroxy hydroperoxides $R_2C(OH)$–OOH,[40] care must be exercised to adopt the appropriate reaction conditions in order to avoid further addition of the α-silyloxy silylperoxide **13** to its parent carbonyl compound (path *ii*). In fact this might lead to α,α'-bis(silyloxy)peroxides, and from these in turn the highly sensitive dimeric 1,2,4,5-tetraoxanes **14** can be formed by way of $(Me_3Si)_2O$ elimination/cyclization (Scheme 4). Actually, by varying reaction conditions the Me_3SiOTf - catalyzed addition of **2** to ketones and aldehydes can be turned into a synthetic method for the preparation of dimeric peroxides **14** (see Section 3.1).[17]

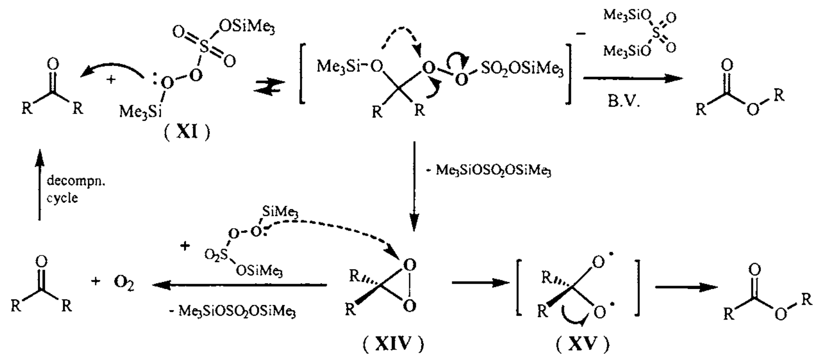
The bis-silyl derivative of Caro's acid **12** provides an interesting variation of the Baeyer–Villiger reaction in that it readily oxidizes aromatic, cyclic, and even simple aliphatic ketones into their corresponding esters in high yields at –20 °C in dichloromethane.[16a] A revisitation[16b] of this reaction showed that an excess of **I** is necessary to bring the transformation to high substrate conversion, and that oxygen gas is evolved; this, coupled with careful ^{18}O-labeling studies,[16b] stringently suggested that the reaction is mediated by formation of dioxiranes[62] (**16**), as shown in Scheme 6.

Of course, the hostile environment does not allow the dioxiranes thus generated to build in any appreciable stationary-state concentration; they either suffer nucleophilic attack by **12** (to yield oxygen gas) or rearrange into esters, most likely via bisoxyl diradicals **16** (Scheme 6).

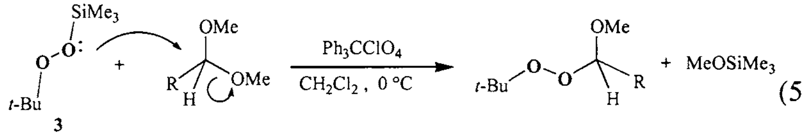
Other than nucleophilic addition to unsaturated moieties, it seems likely that silyl peroxides should be capable of nucleophilic displacement at saturated sp^3 carbon. This is shown by the reaction of *t*-butyl trimethylsilylperoxide **3** with dimethyl acetals, which give rise to α-methoxyalkyl *t*-butyl peroxides (eq. 52).[63]



Scheme 5.



Scheme 6.



(52)

However, the fact that trityl perchlorate was employed as catalyst in the transformation above[63] should warn that this might not proceed by a straightforward, two-electron nucleophilic displacement; in fact, it is quite possible that single-electron transfers mediate the transformation at hand. Careful studies are needed in order to test this hypothesis.

Of course, akin to non-silicon containing peroxides,[40] silyl peroxides might also present the rich reactivity that is characteristic of activation by single-electron transfer in conjunction with suitable donors (or acceptors), including transition metals. At the date of the writing of this review, this realm remains largely unexplored.

8. SILYL TRIOXIDES

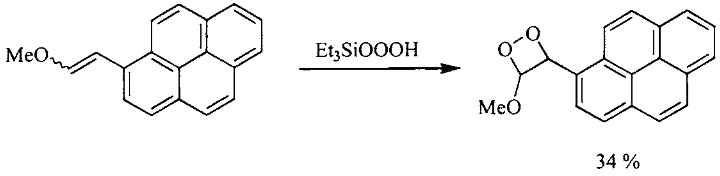
In addition to the silyl peroxides it is possible to synthesize silyl trioxides. Corey and co-workers[64] reported the reaction of triethylsilane with ozone in dichloromethane at dry ice temperature provides triethylsilyl trioxide. This material undergoes thermal decomposition to triethylsilanol and singlet oxygen, $^{1}D_{g}O_{2}$, when warmed to about –60 °C (eq. 53). The half-life for this thermolysis is in the range of 150 s.

$$Et_3SiH + O_3 \xrightarrow[CH_2Cl_2]{-78\ °C} Et_3SiOOOH \xrightarrow[CH_2Cl_2]{-60\ °C} Et_3SiOH + {}^{1}O_2 \qquad (53)$$

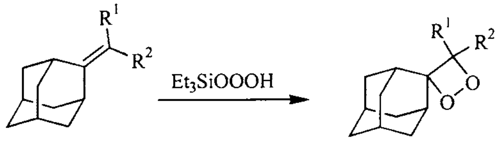
A study of the kinetics of the decomposition of the silyl trioxide in perdeuteroacetone, which showed $\Delta H^{\neq} = 17.2$ kcal mol^{-1} and $\Delta S^{\neq} = +1.6$ cal mol^{-1} s^{-1}, indicates that it proceeds via attack of the γ-oxygen atom on silicon with the elimination of the O_2 molecule. This is very similar to the mechanism for a Peterson olefination from a β-hydroxysilane. By contrast the decomposition of triethylgermyl trioxide, which showed $\Delta H^{\neq} = 17.2$ kcal mol^{-1} and $\Delta S^{\neq} = +1.6$ cal mol^{-1} s^{-1}, is proposed to proceed via attack of the solvent on the proton of the trioxide.[65]

Posner and co-workers[66–68] showed that the decomposition of triethylsilyl trioxide in the presence of electron-rich olefins provides dioxetanes (eqs. 54,55). They have used this reaction in the preparation of some antimalarial trioxanes. With internal disubstituted olefins, triethylsilyl trioxide gives oxidative cleavage, especially when there is oxygen functionality in the molecule (eq. 56).[69]

(54)

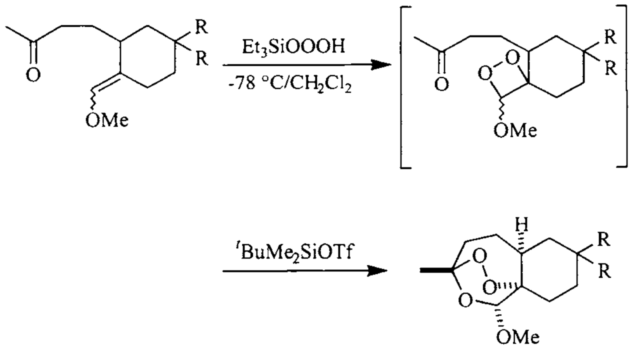


(54)



(55)

R^1,R^2 = MeO, m-OHC_6H_4 (47%); MeO, H (34%); H, Ph (0%)



(56)

R = H (58%); R = Me (42%); R = H, benzyl vinyl ether (48%)

$$n\text{-}C_8H_{17}CH{=}CH(CH_2)_7R \xrightarrow[\text{2) LiAlH}_4]{\text{1) Et}_3\text{SiOOOH}} n\text{-}C_8H_{17}CH_2OH + R(CH_2)_7CH_2OH \qquad (57)$$

$$R = COOMe\ (64\%);\ OAc\ (83\%);\ Me\ (42\%)$$

Ab initio calculations on silyl and carbon trioxides and peroxides were carried out.[70] These studies showed that the binding energies of 6–8 kcal mol^{-1} for the dimerization were sufficiently high to predict that self association through hydrogen bonding was a major contributor to the structure of these materials. The acidities decreased in the order $H_3SiOOOH > H_3COOOH > H_3SiOOH > H_3COOH$. The trioxides donate a proton some 12–13 kcal mol^{-1} more readily than the corresponding peroxides.

Tarunin and co-workers[71] prepared tri-*n*-butylsilyl trioxide and looked at its infrared spectrum. They also investigated the decomposition by proton NMR.

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