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Activation of O₂ by Organosilicon Reagents Yields Quantitative Amounts of H₂O₂ or (Me₃Si)₂O₂ for Efficient O-Transfer Reactions

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Molecular oxygen is kinetically inert and rarely used as a primary oxidant for low temperature selective oxygenation reactions. Here we show that O₂ is converted into H₂O₂ in almost quantitative yields (98%) at ambient temperature and atmospheric pressure in the presence of bis(trimethylsilyl)-1,4-cyclohexadiene (**1**). Similarly, the reaction of O₂ with dihydro-bis(trimethylsilyl) viologen (**2**) and pyrazine (**3**) yields bis(trimethylsilyl) peroxide (BTSP) in excellent yields (up to 99%) at low temperature. Both processes demonstrate that readily available organosilicon reagents enable chemistry typically observed with mono-oxygenase co-enzymes, such as FADH₂ and FMNH₂, in biological systems or at higher pressure via the industrial anthraquinone process. This efficient synthesis of H₂O₂ and BTSP directly from O₂ is particularly attractive for the preparation of the corresponding O-17 and O-18 labelled reagents without the need of large excess amounts of O₂. These are showcased in O-atom transfer reactions to various organic or inorganic substrates, in a two-step one-pot process, making the rapid and on-demand synthesis of large libraries of O-labelled compounds readily possible.

Keywords: H₂O₂ o BTSP o O₂ activation o O-labelling o Organosilicon agents

Introduction

Oxygenation is one of the most fundamental chemical transformations, with key applications in industrial processes. Ideally, O₂ is the most atom-economical and environmentally friendly oxidant.^[1-3] Besides the oxidation of alcohols, O₂ is however rarely used as a primary oxidant in low temperature homogeneous oxygenation processes as a consequence of its kinetically inert triplet ground state. Most processes still rely on ROOH, H₂O₂, or related compounds such as peracids,^[4] bis(trimethylsilyl)peroxide (BTSP)^[5] and urea-H₂O₂ (UHP)^[6]. In nature, O₂ activation is accomplished by (mono- or di-)oxygenases, wherein riboflavin-based coenzymes activate O₂ to form an hydroperoxide intermediate. These activated forms of O₂ are then used in oxygen-atom transfer in reactions such as phenol hydroxylation, Baeyer-Villiger oxidation, olefin epoxidation, hypochlorite formation (Scheme 1a).^[7] Analogously, in industrial processes O₂ is reacted with hydrocarbons to generate alkyl hydroperoxide intermediates or transformed into H₂O₂ via the anthraquinone process (Scheme 1b)^[8, 9], although the direct synthesis of H₂O₂ from H₂ and O₂ gases has been an active area of research for a few decades.^[10] In the anthraquinone process, dihydroanthraquinone, which is generated by hydrogenation of anthraquinone, undergoes autoxidation with O₂ to generate H₂O₂. This oxidant is used in

Scheme 1. A representative scheme of the mono-oxygenation reaction using O₂ as the oxygen atom source with typical (a-b) and proposed (this work, c) O₂ activators, the corresponding peroxides, and byproducts that form during the mono-oxygenation process.

	O ₂ Activators	Peroxides	Byproducts
a) Natural: Riboflavin-based monoxygenase system			
b) Industrial (state of the art): The anthraquinone process		H ₂ O ₂	
c) This work: Organosilicon reagents	 	H ₂ O ₂ (Me ₃ Si) ₂ O ₂ (Me ₃ Si) ₂ O ₂	

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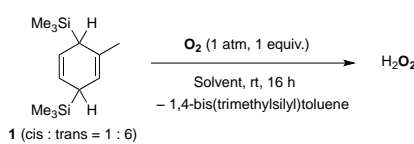
paper bleaching and industrial organic synthesis, the latter typically in combination with transition-metal catalysts in homogeneous or heterogeneous phases for selective oxidation reactions, including for the large-scale production of propylene oxide from propylene using titanium-silicalites as catalysts.^[11]

Both biological and the industrial processes rely on a common aromatization-dearomatization recursive sequence as a key step for dioxygen activation and reduction. We thus reasoned that organosilicon reagents such as 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (**1**), N,N'-bis(trimethylsilyl)-4,4'-dihydropyridine (**2**), and N,N'-bis(trimethylsilyl)-2,3,5,6-tetramethyldihydropyridazine (**3**), which are readily available and efficient reducing reagents for a broad range of organic and inorganic derivatives,^[12-16] could constitute useful and convenient reagents to produce X₂O₂ (X = H and SiMe₃) from O₂, the primary oxidant (Scheme 1c).

Results and Discussion

We first focused on using a trimethylsilyl-substituted 1,4-cyclohexadiene derivative **1** to convert O₂ into H₂O₂. Reaction of **1** with 1 equivalent of O₂ in a bi-phasic solution of CH₂Cl₂/H₂O produces H₂O₂ in up to 81% yield (entry 1-4, Table 1). The only detected byproduct is 1,4-bis(trimethylsilyl)toluene (96% recovered), which is dissolved in the CH₂Cl₂ layer and can be easily separated from H₂O₂ in the water layer. Other biphasic solvent combinations can be used such as toluene/H₂O (entry 5) and MTBE/H₂O (entry 6), or alternatively water alone (entry 7). The presence of H₂O is necessary to obtain H₂O₂ in good yield from **1** in nonpolar solvents (entry 1 vs. entry 4). When using polar solvents such as t-butanol (entry 8), CH₃CN (entry 9), NMP (entry 10), and THF (entry 11), H₂O₂ is generated in excellent yields (up to 98%) in all cases. Synthetic air (gas mixture of 20% O₂ and 80% N₂) can be also used to generate H₂O₂ with good selectivity, although the rate of the reaction decreases, leading to a

Table 1. H₂O₂ formation by the reaction of **1** with O₂.



Entry	Solvent	Yield(%) of H ₂ O ₂
1	CH ₂ Cl ₂ (9 mL) / H ₂ O (1 mL)	81
2	CH ₂ Cl ₂ (9 mL) / H ₂ O (0.4 mL)	80
3	CH ₂ Cl ₂ (9 mL) / H ₂ O (0.1 mL)	74
4	CH ₂ Cl ₂ (9 mL)	40
5	toluene (9 mL) / H ₂ O (1 mL)	79
6	MTBE (9 mL) / H ₂ O (1 mL)	75
7	H ₂ O (10 mL)	78
8	t-butanol (9 mL)	93
9	CH ₃ CN (9 mL)	98
10	NMP (9 mL)	97
11	THF (9 mL)	88
12 ^a	CH ₂ Cl ₂ (9 mL) / H ₂ O (1 mL)	46 ^b

^a The reaction is carried out under flow of synthetic air (1 atm).

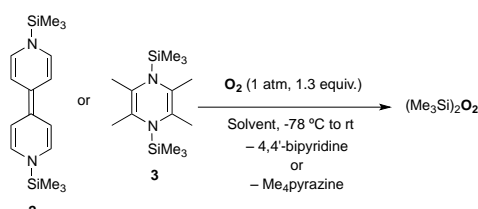
^b The conversion of **1** is 50%.

lower yield (entry 12). In sharp contrast to **1**, 1,4-cyclohexadiene does not provide H₂O₂ under otherwise identical reaction conditions, indicating that the trimethylsilyl groups located at the allylic position in **1** are essential for high reactivity and/or selectivity (entry 1, Table S2).^[17, 18] It is noteworthy that **1** does not react with H₂O₂ under the conditions described here, which enable us to obtain H₂O₂ in a high yield and selectivity. This method is particularly interesting in the laboratory scale and to synthesize isotopically labeled compound (vide infra), because it does not require the use of large excess of O₂ and/or autoclave.^[19-22] Although 1,2-diphenylhydrazine is reported to generate H₂O₂ under continuous bubbling of O₂ at ambient condition, the reaction with a stoichiometric amount of O₂ gives H₂O₂ in lower yield than **1** (entry 2, Table S2).^[23]

Replacing organosilicon reagent **1** with **2** or **3** allows, in the absence of water, for the transfer of two trimethylsilyl groups to O₂, yielding directly bis(trimethylsilyl)peroxide (BTSP), which is a water(proton)-free analogue of H₂O₂ and a highly efficient BT source of oxygen atom in O-transfer reactions such as epoxidation, N-oxide formation, Baeyer Villiger oxidation, and sulfoxidation (Table 2).^[24-28] For instance, the reaction of **2** with O₂ (1.3 equiv.) in CH₂Cl₂ at -78 °C produces BTSP in nearly quantitative yield (99%) along with 4,4'-bipyridine (entry 1), which can be separated by trap-to-trap vacuum distillation to give a BTSP solution in CH₂Cl₂ (0.39 M). This reaction can be carried out in a broad range of solvents such as toluene, pentane, Et₂O, THF, giving solutions of BTSP in quantitative yield in the corresponding solvents (entries 2-5). Similarly, the reaction of **3** with O₂ (1.3 equiv.) in CH₂Cl₂ affords BTSP in 93% yield along with tetramethylpyridazine (entry 6). A small amount of hexamethyldisiloxane and octamethyltrisiloxane, which are generated by a side reaction of BTSP with **2** or **3**, are also detected by NMR spectroscopy and GC-MS. The formation of these siloxane byproducts increases when using sub-stoichiometric amounts of O₂ or when the reaction is carried out at room temperature.

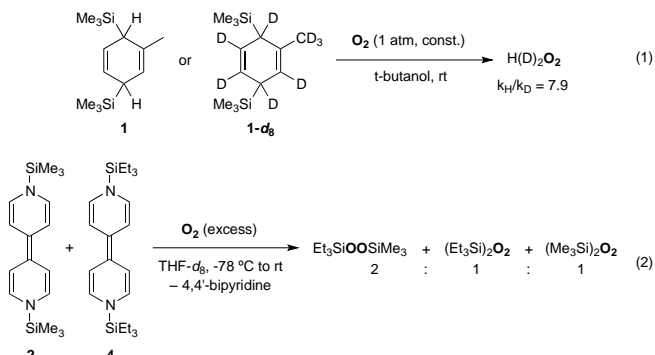
We also examined the reaction of **1-d₈** and **1** with O₂. The use of **1-d₈** provides access to D₂O₂, and comparison of the kinetics of both reactions shows a kinetic isotope effect – k_H/k_D (KIE) – of 7.9 in t-butanol, which

Table 2. BTSP formation by the reaction of **2** or **3** with O₂.



Entry	Reductant	Solvent	Yield(%) of (Me ₃ Si) ₂ O ₂
1	2	CH ₂ Cl ₂	99
2	2	C ₆ H ₆	99
3	2	Et ₂ O	99
4	2	THF	99
5	2	pentane	99
6	3	CH ₂ Cl ₂	93

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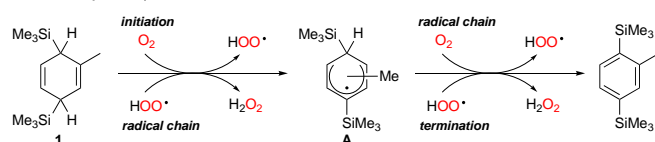


indicates that the abstraction of allylic hydrogen is involved in the rate determining step (eq. 1 and Fig. S1).

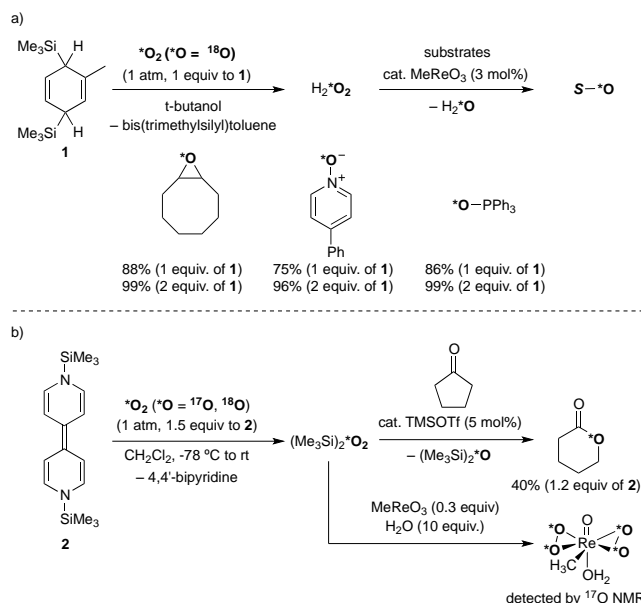
To further probe the reaction mechanism, we have also investigated this reaction in the presence of various amount of 2,6-tBu-4-Me-phenol, up to 1 equiv, as a radical trapping agent. Under these conditions, **1** was consumed to the extent of only 2% in the presence of 2,6-tBu-4-Me-phenol (1 mol%) after 2 hours, while higher amount of 2,6-tBu-4-Me-phenol (10-100 mol%) lead to no conversion, suggesting the involvement of a radical chain mechanism (Fig. S2). Noteworthy, the reaction of **2** and its bis(trimethylsilyl) analogue **4** (1:1) with excess of O₂ yields Et₃SiOOSiMe₃ as well as (Me₃Si)₂O₂ and (Et₃Si)₂O₂ in a 2:1:1 ratio (eq. 2 and Fig S3). The same products are observed when pyrazine-based compounds, **3** and its bis(trimethylsilyl) analogue, are used (Scheme S1). Et₃SiOOSiMe₃ is not formed by mixing a solution of (Me₃Si)₂O₂ and (Et₃Si)₂O₂ in the presence of 4,4'-bipyridine. These results indicate that Et₃SiOOSiMe₃ is generated during the O₂ activation process, and trialkylsilyl groups are transferred in a stepwise fashion to the O₂ fragment via the formation of mono(trialkylsilyl)peroxide species.

All data point to a reaction mechanism involving a radical chain mechanism as shown in Scheme 2.^[17] The reaction between **1** and O₂ probably leads to the radical intermediate **A**, via a direct H-abstraction or through a single-electron transfer (SET) as proposed for other reducing agent (vide infra). The radical chain continues with the reaction of hydroperoxy radical with **1**, and **A** with O₂. Termination takes place with the reaction of hydroperoxy radical and **A** to generate hydrogen peroxide and 1,4-bis(trimethylsilyl)toluene. The presence of trimethylsilyl groups^[29] and two olefins is probably important to stabilize the radical intermediate **A**. The concerted abstraction of the two allylic hydrogens of **1** with O₂ may be ruled out because trans-**1** is also converted at almost the same reaction rate. For BTSP, the transfer of trimethylsilyl group of **2** and **3** to the O₂ fragment probably takes place sequentially and involves a SET process (Scheme S1). The faster formation of BTSP than H₂O₂ is consistent with a SET process since **2** and **3** possess more negative redox potential than **1** and are able to reduce acceptor molecules like tetracyanoethylene (TCNE)

Scheme 3. (a) Generation of O-18 H₂O₂ and subsequent oxidation to produce labeled oxygen incorporated compounds. (b) Generation of O-17 or O-18 (Me₃Si)₂O₂ and subsequent Baeyer-Villiger type oxidation and preparation of MeRe(=O)(¹⁷O)₂(OH)₂.



Scheme 3. (a) Generation of O-18 H₂O₂ and subsequent oxidation to produce labeled oxygen incorporated compounds. (b) Generation of O-17 or O-18 (Me₃Si)₂O₂ and subsequent Baeyer-Villiger type oxidation and preparation of MeRe(=O)(¹⁷O)₂(OH)₂.



Formation of trimethylsilyl radical can be ruled out in this system since the trimethylsilyltoluene and/or bis(trimethylsilyl)toluene isomers are not observed in the reaction mixture.^[32]

The method we have described to prepare H₂O₂ and BTSP from O₂ is particularly convenient in a laboratory scale, especially for the preparation of O-17 and O-18 labeled X₂O₂ compounds (X = H, D, and SiMe₃), because the reaction proceeds in high yield with only a stoichiometric or slight excess amount of O₂. For instance, H₂O₂ generated in situ is readily used to prepare a broad range of labeled organic and inorganic compounds – Scheme 3. As illustrative examples, we demonstrate the preparation of the O-18 labeled cyclooctene oxides, 4-phenylpyridine N-oxide, and triphenylphosphine oxide using MeReO₃ as a catalyst from O-18 H₂O₂, and δ-valerolactone via the Baeyer-Villiger oxidation from O-18 BTSP.^[33,34] The ¹⁷O NMR spectrum of the reaction mixture of **2** with ¹⁷O₂ in CD₂Cl₂ shows a broad signal at 216.8 ppm for O-17 labeled BTSP. The generated O-17 labeled BTSP can be used to generate O-17 labeled bis(peroxo) rhenium complex, MeRe(=O)(¹⁷O)₂(OH)₂, which show O-17 signals at 420.1 and 364.8 ppm in CD₂Cl₂.

Conclusions

We have developed a straightforward method to produce H₂O₂ and BTSP by the reaction of organosilicon reducing reagents with O₂. This method only requires stoichiometric amounts of reagents (no excess of O₂) and is thus particularly useful for rapid and on-demand synthesis of the corresponding O-17 and O-18 labeled compounds, which can be then used to install labeled oxygen in organic and inorganic substrates. This work also shows that riboflavin co-enzymes – essential for the activation of O₂ in mono-oxygenase processes found in nature – can be replaced by organosilicon reagents, which are readily prepared on multi-gram scale, in a simple reaction flask used in synthetic chemistry laboratories.

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Supplementary Material

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/MS-number>.

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Author Contribution Statement

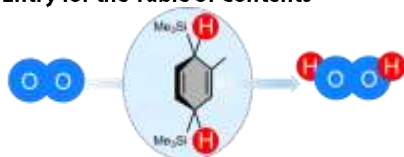
K. Y. conducted the research investigation with the help of S. T. and H. H. K. Y., S. T., H. T., K. M., and C. C. analyzed the results and wrote the manuscript.

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Entry for the Table of Contents



EASY and SAFE Preparation of H_2O_2 for a laboratory scale

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A new synthetic route to prepare environmentally friendly oxidant, H_2O_2 , from stoichiometric amount of O_2 and organosilicon reducing agent.