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Cobalt-Catalyzed Intramolecular Silylperoxidation of Unsaturated Diisopropylsilyl Ethers

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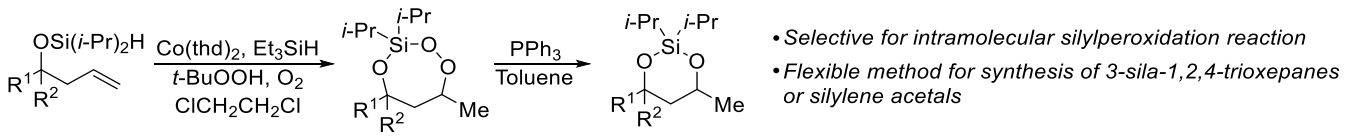
Supporting Information Placeholder

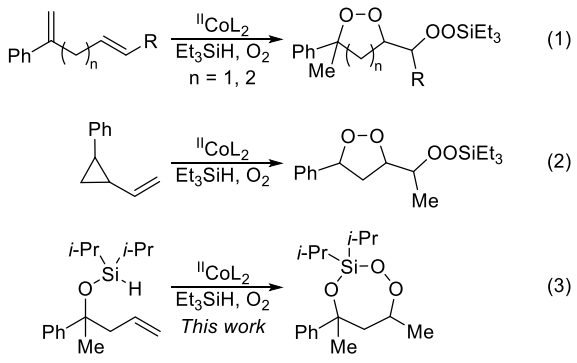


ABSTRACT: A cobalt-catalyzed intramolecular silylperoxidation reaction was developed that allows for the conversion of unsaturated diisopropylsilyl ethers to 3-sila-1,2,4-trioxepanes. Reduction of the peroxide unit of the 3-sila-1,2,4-trioxepane yields six-membered ring diisopropylsilylene acetals.

INTRODUCTION

The cobalt-catalyzed oxygenation of alkenes is an effective reaction for the synthesis of silyl peroxides,[1] but can also be applied to the synthesis of a variety of endoperoxides,[2] including 1,2-dioxolanes,[3,4,5] 1,2-dioxanes,[4,6] 1,2-dioxepanes,[7] and 1,2,4-trioxolanes.[8,9] The reaction, which converts alkenes to silyl peroxides through a peroxyl radical intermediate,[1,10,11] uses a cobalt(II) catalyst, molecular oxygen, and a silane reducing agent. Depending on the choice of substrate, the peroxyl radical intermediate can react intramolecularly, forming endoperoxides instead. Treatment of either a 1,4- or 1,5-diene[4,12] with the cobalt-catalyzed oxygenation conditions resulted in the formation of 1,2-dioxolanes and 1,2-dioxanes, respectively (Scheme 1, eq 1). Similar reactivity was observed with vinylcyclopropanes, which formed 1,2-dioxolanes (Scheme 1, eq 2).[3,12] In this Article, we report that unsaturated diisopropylsilyl ethers can undergo an intramolecular silylperoxidation reaction to form 3-sila-1,2,4-trioxepanes (Scheme 1, eq 3).[13] Upon reduction of the peroxide unit using triphenylphosphine, the corresponding silylene-protected 1,3-diol was formed.

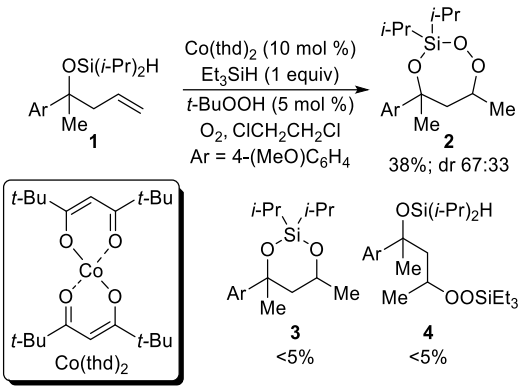
Scheme 1. Co-Catalyzed Endoperoxide Formation



RESULTS AND DISCUSSION

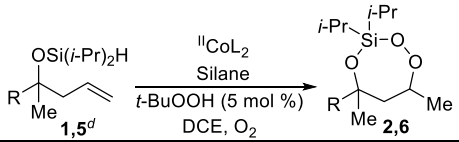
During our investigation into new applications of the cobalt-catalyzed oxygenation of alkenes, we found that intramolecular silylperoxidation can be achieved. When unsaturated diisopropylsilyl ether **1** was subjected to cobalt-catalyzed oxygenation (Scheme 2), after less than an hour, 3-sila-1,2,4-trioxepane **2** was formed as the major product. In addition, trace amounts of diisopropylsilylene acetal **3** and linear silyl peroxide **4** were detected by ^{1}H NMR spectroscopy. Formation of 3-sila-1,2,4-trioxepane **2** as the major product was not anticipated because the silylation step of the cobalt-catalyzed oxygenation of alkenes is generally sensitive to both the steric and electronic environment of the silane.[14,15] In this case, however, the diisopropylsilyl group was preferentially incorporated into the peroxide. The above observation was significant because, for comparison, the synthesis of a triisopropylsilyl peroxide using the cobalt-catalyzed oxygenation of alkenes is very difficult considering the poor reactivity of triisopropylsilane.[14,16]

Scheme 2. Products of Co-Catalyzed Intramolecular Silylperoxidation of Unsaturated Diisopropylsilyl Ethers



The yield of the 3-sila-1,2,4-trioxepane was found to be sensitive to the choice of the added silane and cobalt catalyst. When unsaturated diisopropylsilyl ether **5** was subjected to cobalt-catalyzed oxygenation using $Co(acac)_2$, triethylsilane, and catalytic *tert*-butyl hydroperoxide (Table 1, entry 1), 3-sila-1,2,4-trioxepane **6** was isolated in 21% yield. Triethylsilane and *tert*-butyl hydroperoxide were required to initiate the reaction rapidly.[3] The use of a more sterically bulky silane (Table 1, entries 2 and 3) or one with electron withdrawing groups (Table 1, entry 4) gave only trace product formation after 20 h. The poor reactivity of these silanes can be explained by considering that formation of the reactive cobalt-hydride species is sensitive to the choice of silane.[3,14] When $Co(thd)_2$ was used instead of $Co(acac)_2$, decreased reaction times and increased yields were observed (Table 1, entries 6–8). The combination of $Co(thd)_2$ with catalytic phenylsilane (Table 1, entry 7) or stoichiometric triethylsilane (Table 1, entry 8) resulted in the greatest yields of the 3-sila-1,2,4-trioxepane. Optimized reaction conditions were achieved using 10 mol % $Co(thd)_2$ and one equivalent of triethylsilane,[17] which yielded the 3-sila-1,2,4-trioxepane **2** in 74% yield, as determined by ^{1}H NMR spectroscopy (Table 1, entry 8). The isolated yield of **2**, however, was only 38% (Table 1, entry 8), suggesting that the 3-sila-1,2,4-trioxepane was not stable to column chromatography.[18]

Table 1. Optimization of Co-Catalyzed Intramolecular Silylperoxidation of Unsaturated Diisopropylsilyl Ethers

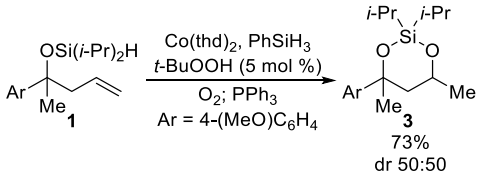


Entry	R	$^{II}CoL_2$ (mol %)	Silane (equiv)	time (h)	yield[a] (NMR)
1	Ph	acac (20)	Et_3SiH (2)	1.5	21%[b]
2	Ph	acac (20)	$(i\text{-Pr})_3SiH$ (2.5)	20	trace
3	Ph	acac (20)	Ph_3SiH (2.5)	20	trace
4	Ph	acac (20)	$(EtO)_3SiH$ (2.5)	20	trace
5	Ph	acac (20)	Ph_2MeSiH (2)	3	34%
6	Ph	thd (12)[c]	Ph_2MeSiH (1)	2	67%
7	4-(MeO)C_6H_4	thd (16)	$PhSiH_3$ (0.16)	0.75	74%
8	4-(MeO)C_6H_4	thd (10)	Et_3SiH (1)	0.75	74% (38%)[b]

[a]Yield determined by ^{1}H NMR spectroscopy with mesitylene as the internal standard. [b]Isolated yield. [c]thd = 2,2,6,6-tetramethyl-3,5-heptanedionato. [d]**1**,**2**, R = 4-(MeO)C_6H_4; **5**,**6**, R = Ph.

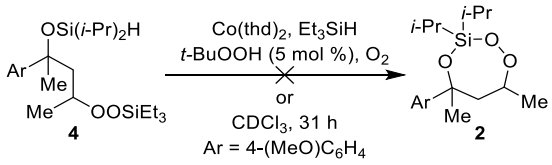
Reducing the 3-sila-1,2,4-trioxepane to the corresponding diisopropylsilylene acetal provided a product that was more stable to purification.[19,20] After the cobalt-catalyzed oxygenation was completed, the peroxide unit of 3-sila-1,2,4-trioxepane **2** was reduced using triphenylphosphine.[21,22] The above modification to the procedure resulted in a 73% isolated yield of diisopropylsilylene acetal **3** over two steps (Scheme 3). When the cobalt-catalyzed oxygenation was performed using triethylsilane instead of phenylsilane, the isolated yield of diisopropylsilylene acetal **3** decreased slightly to 60% due to the formation of trace amounts of linear silyl peroxide **4** (Scheme 2).[14,23] Linear silyl peroxide **4** can be difficult to separate from diisopropylsilylene acetal **3**.

Scheme 3. Formation of Diisopropylsilylene Acetal 3 from 3-Sila-1,2,4-Trioxepane 2



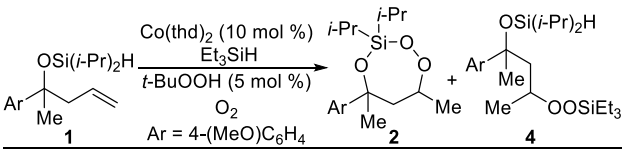
Several control experiments yielded insight into the reaction mechanism. The first experiment was aimed at determining whether the 3-sila-1,2,4-trioxepane could form through a mechanism involving migration of the peroxide between the silicon atoms (Scheme 4). When linear silyl peroxide **4** was resubjected to the reaction conditions, none of the 3-sila-1,2,4-trioxepane **2** was observed by ^{1}H NMR spectroscopy after 19 h. Even when a pure sample of linear silyl peroxide **4** was allowed to stand in deuterated chloroform, formation of 3-sila-1,2,4-trioxepane **2** was not observed.

Scheme 4. Exchange of Silanes Not Observed



Other control experiments were designed to determine the role of triethylsilane. One hypothesis was that the triethylsilane catalyzed the initial formation of the cobalt-hydride species. When unsaturated diisopropylsilyl ether **1** was subjected to the reaction conditions without the addition of triethylsilane, formation of 3-sila-1,2,4-trioxepane **2** occurred slowly over the course of 19 h, with a final yield of 37% by ^{1}H NMR spectroscopy (Table 2, entry 1). With the addition of one equivalent of triethylsilane, the reaction was completed in 0.5 h with a 74% yield of 3-sila-1,2,4-trioxepane **2** by ^{1}H NMR spectroscopy (Table 2, entry 2). These data suggested that triethylsilane was necessary to catalyze the formation of the cobalt-hydride species and that the diisopropylsilyl group alone was not kinetically competent enough to do so. Even with a large excess of triethylsilane (Table 2, entries 3 and 4), formation of 3-sila-1,2,4-trioxepane **2** was competitive with the formation of linear silyl peroxide **4**.

Table 2. Equivalents of Triethylsilane and Effect on Product Distribution

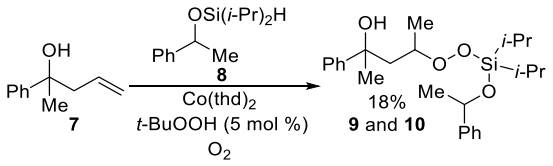


Entry	Et_3SiH (equiv)	time (h)	conversion of **1**	yield **2**[a] (NMR)	yield **4**[a] (NMR)
1	-	19	68%	37%	-
2	1	0.5	100%	74%	5%
3	10	0.5	100%	43%	39%
4	20	0.5	100%	37%	50%

[a]Yield determined by ^{1}H NMR spectroscopy with mesitylene as the internal standard.

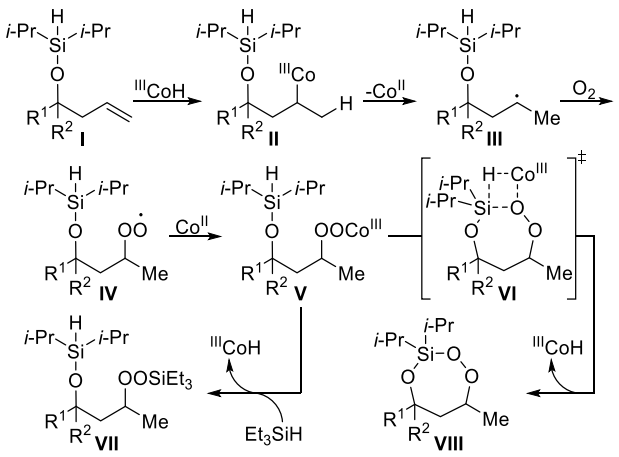
Further evidence of triethylsilane's role was observed when alcohol **7** and diisopropylsilane **8** were subjected to the cobalt-catalyzed oxygenation (Scheme 5). The purpose of this experiment was to confirm that the diisopropylsilyl group alone cannot sufficiently initiate the reaction. With two equivalents of diisopropylsilane **8**, even after 22 h, the conversion of **7** was low and the yield of diastereomers **9** and **10** was 18% (Scheme 5). This observation, combined with the data in Table 2, entry 1, indicates that the addition of triethylsilane is required to initiate the reaction.

Scheme 5. Co-Catalyzed Silylperoxidation Using Diisopropylsilane 8



A mechanism can be proposed that is consistent with the above observations (Scheme 6). The first step in this mechanism is the formation of a cobalt-hydride species, which is catalyzed by *tert*-butyl hydroperoxide[24] and triethylsilane.[3,25] Addition of the cobalt-hydride species across the double bond of a molecule of unsaturated diisopropylsilyl ether **I**, followed by dissociation of the cobalt catalyst from **II**, would form alkyl radical **III**. The addition of cobalt-hydride occurs in such a way as to generate the more substituted radical intermediate.[3,14] Alkyl radical **III** can react with molecular oxygen, forming peroxyl radical **IV**, which, upon coordination to cobalt, yields Co(III)–peroxyl intermediate **V**.[4] Co(III)–peroxyl intermediate **V** can react by one of two ways. The first pathway involves an intramolecular transmetalation reaction (**VI**) between Co(III)–peroxyl intermediate **V** and the diisopropylsilyl group,[3] resulting in formation of 3-sila-1,2,4-trioxepane **VIII**. The formation of other seven-membered ring products involving a transition state analogous to **VI** have been reported.[26,27] The alternative pathway is also a transmetalation reaction, but instead occurs between Co(III)–peroxyl intermediate **V** and triethylsilane, yielding linear silyl peroxide **VII**. The mechanism of formation of 3-sila-1,2,4-trioxepane **VIII** is different from that of other intramolecular endoperoxide forming reactions (Scheme 1, eqs 1 and 2) in that product formation occurs from Co(III)–peroxyl intermediate **V** instead of peroxyl radical **IV**. It was suspected that because triethylsilane was only incorporated into less than 5% of the product (Scheme 2), any remaining triethylsilane either remained unreacted[28] or was oxidized.[3]

Scheme 6. Proposed Mechanism for the Co-Catalyzed Intramolecular Silylperoxidation of Unsaturated Diisopropylsilyl Ethers



The cobalt-catalyzed intramolecular formation of 3-sila-1,2,4-trioxepanes was general for several unsaturated diisopropylsilyl ethers (Table 3).[29] Unsaturated silyl ethers **1** and **12**–**15** (Table 3)[30] were synthesized by addition of a Grignard reagent to a carbonyl compound followed by silylation of the resulting alcohol, as outlined for diisopropylsilyl ether **15** in Scheme 7. There was a correlation between the degree of substitution of the alkene substrate and its reactivity in the intramolecular silylperoxidation.[4] When monosubstituted alkenes **1**, **12**, and **13** were subjected to the cobalt-catalyzed oxygenation, the reaction was completed in two hours or less (Table 3, entries 1–3). Di-substituted alkene **14** required heating and a longer reaction time, ultimately yielding diisopropylsilylene acetal **18** in 39% (Table 3, entry 4). The added substitution at the allylic position of unsaturated silyl ether **15** also resulted in the need for heating and a longer reaction time (Table 3, entry 5). Unsaturated silyl ether **15** (Table 3, entry 5) gave the highest diastereomeric ratio out of all of the unsaturated silyl ethers tested. Generally, when a more sterically hindered alkene undergoes cobalt-catalyzed oxygenation, diastereoselectivity increases.[31,32,33]

In some examples (Table 3, entries 3–5), $Co(acac)_2$ was used instead of $Co(thd)_2$ to facilitate the purification process. During the course of the cobalt-catalyzed oxygenation, $Co(thd)_2$ was converted to $Co(thd)_3$,[34,35] which can be difficult to separate from the diisopropylsilylene acetal product during column chromatography. Difficulties with the purification process using similar cobalt catalysts has been reported.[36] Even though $Co(acac)_2$ improves the purification process, $Co(thd)_2$ was the better catalyst for these cobalt-catalyzed intramolecular silylperoxidation reactions. Compared to $Co(acac)_2$, $Co(thd)_2$ generally resulted in better yields of the 3-sila-1,2,4-trioxepane, shorter reaction times, and better conversion of the starting material.

The degree of substitution of the diisopropylsilyl ether affected the stability of the products from the cobalt-catalyzed intramolecular silylperoxidation. For example, secondary benzylic silyl ether **12** yielded the least amount of diisopropylsilylene acetal **16** (Table 3, entry 2).[37] Diisopropylsilylene acetal **16** was also found to be sensitive to purification. Prior to chromatography, analysis of the crude reaction mixture of diisopropylsilylene acetal **16** showed a diastereomeric ratio of 40:60, however, after purification, only the minor diastereomer of **16** was isolated. By comparing the ^{1}H and ^{13}C NMR chemical shifts and coupling constants of diisopropylsilylene acetal **16** to structurally similar diisopropylsilylene acetals,[38] it was determined that the *syn* diastereomer of **16** was isolated. Decomposition of diisopropylsilylene **16** had occurred during chromatography as evident by the formation of 1,3-diol **20** as a mixture

of diastereomers (Table 3, entry 2). Decreased stability of benzylic diisopropylsilylene acetals has been previously observed.[39]

Scheme 7. Synthesis of Unsaturated Diisopropylsilyl Ethers

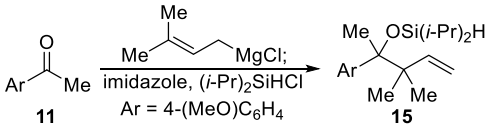
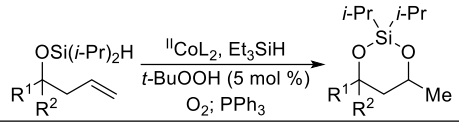
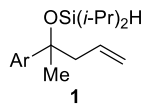
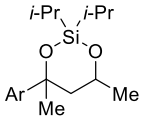
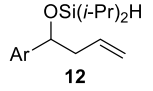
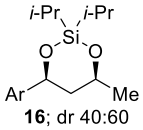
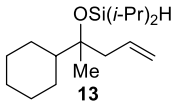
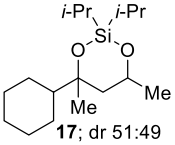
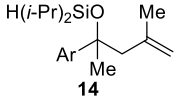
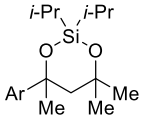
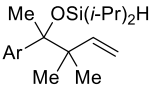
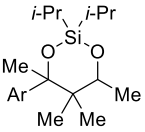
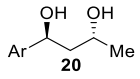


Table 3. Unsaturated Silyl Ether Screen



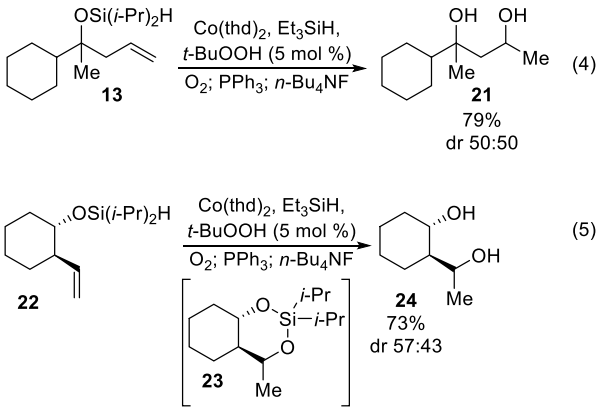
Entry	unsaturated silyl ether[a]	$^{II}CoL_2$ (mol %)	time (h)	silylene acetal	yield
1	 **1**	$Co(thd)_2$ (10)	0.5	 **3**; dr 51:49	60%
2	 **12**	$Co(thd)_2$ (10)	1	 **16**; dr 40:60	15%[c]
3	 **13**	$Co(acac)_2$ (40)	2	 **17**; dr 51:49	62%
4	 **14**	$Co(acac)_2$ (40)	3[b]	 **18**	39%
5	 **15**	$Co(acac)_2$ (40)	5[b]	 **19**; dr 70:30	32%

[a]Ar = 4-(MeO)C_6H_4. [b]Reaction heated to 40 °C for this time. [c]1,3-Diol **20** was formed in 21% yield as a 67:33 mixture of diastereomers.



Removal of the diisopropylsilylene acetal protecting group using tetrabutylammonium fluoride yielded the corresponding diol, which was generally easier to purify. For example, attempts to purify diisopropylsilylene acetal **17** by chromatography (Table 3, entry 3), when the cobalt-catalyzed oxygenation was performed using $Co(thd)_2$, were unsuccessful because of trace amounts of $Co(thd)_3$ co-eluting with diisopropylsilylene acetal **17**. By contrast, when the crude diisopropylsilylene acetal was treated with tetrabutylammonium fluoride (Scheme 8, eq 4), 1,3-diol **21** was isolated in 79% yield over three steps (Scheme 8, eq 4). Similarly, diisopropylsilylene acetal **23** was unstable to column chromatography and could not be purified (Scheme 8, eq 5). Treatment of a crude diisopropylsilylene acetal **23** with tetrabutylammonium fluoride yielded 1,3-diol **24** in 73% over three steps.

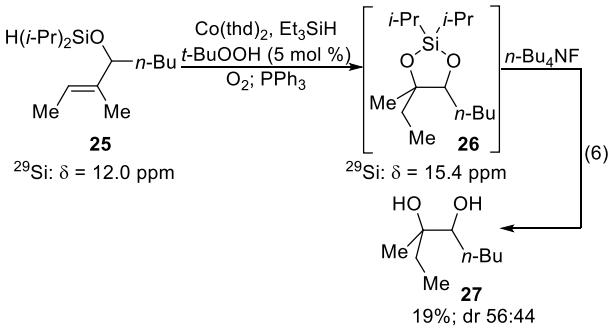
Scheme 8. Deprotection of Diisopropylsilylene Acetals



The cobalt-catalyzed oxygenation of unsaturated diisopropylsilyl ethers could also be applied to the synthesis of five-membered ring diisopropylsilylene acetals (Scheme 9, eq 6). Unsaturated diisopropylsilyl ether **25** formed five-membered diisopropylsilylene acetal **26** (Scheme 9, eq 6) upon treatment with the cobalt-catalyzed oxygenation and subsequent reduction of the peroxide. This product, however, was not stable to purification by column chromatography.[20] Its formation was suggested by ^{29}Si NMR spectroscopy, which showed that not only had the chemical shift of diisopropylsilylene acetal **26** changed compared to that of the starting material (**25**), but also that this new chemical shift was within the range of other five-membered ring silylene acetals (Scheme 9, eq 6).[40,41] These observations were confirmed by demonstrating that treatment of diisopropylsilylene acetal **26** with tetrabutylammonium fluoride yielded the corresponding 1,2-diol (**27**) in 19% over three steps (Scheme 9, eq 6).

Synthesis of a seven-membered ring diisopropylsilylene acetal was not successful (Scheme 9, eq 7). When unsaturated diisopropylsilyl ether **28** was subjected to the cobalt-catalyzed oxygenation, no cyclization product was observed. Instead, only linear silyl peroxide **29** (Scheme 9, eq 7) was formed. As the distance between the alkene and diisopropylsilyl group increases, formation of the linear silyl peroxide becomes the favored reaction pathway instead of intramolecular cyclization (Scheme 6).

Scheme 9. Ring Size Screen for the Co-Catalyzed Intramolecular Silylperoxidation of Unsaturated Diisopropylsilyl Ethers



CONCLUSION

In summary, we have demonstrated that an intramolecular silylperoxidation reaction can be applied to the synthesis of 3-sila-1,2,4-trioxepanes from unsaturated diisopropylsilyl ethers. With the use of triphenylphosphine, the peroxide unit of the 3-sila-1,2,4-trioxepane can be reduced to yield diisopropylsilylene acetals. A mechanism has been suggested in which the addition of triethylsilane was necessary in order to initiate the reaction. The key intermediate of this reaction is a Co(III)–peroxyl intermediate, which can either react intra- or intermolecularly. Intramolecular formation of the 3-sila-1,2,4-trioxepane is favored over the intermolecular reaction, which forms the triethylsilyl peroxide instead. Formation of the 3-sila-1,2,4-trioxepane does not involve a silane-exchange pathway, but, an intramolecular transmetalation reaction cannot be ruled out. More sterically hindered alkenes yielded less of the diisopropylsilylene acetal. Removal of the diisopropylsilylene acetal group was achieved using tetrabutylammonium fluoride, which yields the corresponding diol.

EXPERIMENTAL SECTION

General Information. All ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature at 400, 500, and 600 MHz, or 100, 125, and 150 MHz, respectively. The data were reported as follows: chemical shifts reported in parts per million from residual solvent peaks (^{1}H NMR $CDCl_3$ δ 7.26, C_6D_6 δ 7.16; ^{13}C NMR $CDCl_3$ δ 77.23, C_6D_6 δ 128.4) on the δ scale, multiplicity (s, singlet; br, broad; d, doublet; t, triplet; q, quartet; quint, quintet; dd, doublet of doublets; m, multiplet), coupling constants (hertz), and integration. The multiplicity of carbon peaks was determined using HSQC or DEPT experiments. Infrared (IR) spectra were recorded using attenuated total reflectance (ATR). High-resolution mass spectra (HRMS) were recorded using a time-of-flight spectrometer with atmospheric-pressure chemical ionization (APCI) or electrospray ionization (ESI) ionization sources. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on silica gel (SiO_2) 60 Å (230−400 mesh) unless noted, otherwise, aluminium oxide (Al_2O_3), neutral, Brockmann I, particle size 50-200 μm, 60 Å was used. THF and Et_2O were dried and degassed using a solvent purification system before being used. All reactions were performed under a nitrogen atmosphere in glassware that had been flame-dried under vacuum unless otherwise stated. All reactions that were performed under an oxygen atmosphere used glassware that was not flame-dried. Unless otherwise noted, all reagents were commercially available. Prenylmagnesium chloride was prepared by known methods.[42] $Co(acac)_2$ was prepared by known methods.[43] The following alcohols were prepared by known methods: 2-phenylpent-4-en-2-ol (**7**),[44] 1-(4-methoxyphenyl)but-3-en-1-ol,[45] 2-(4-methoxyphenyl)hex-5-en-2-ol,[46] *trans*-2-vinylcyclohexan-1-ol,[47] and (*E*)-3-methyloct-2-en-4-ol.[48] Diisopropylsilyl ether **8** was prepared by known methods.[49]

Synthesis of Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(II) ($Co(thd)_2$).

The synthesis of $Co(thd)_2$ was performed using a modified reported procedure.[34] Ammonium hydroxide (50% v/v aqueous solution, 0.63 mL, 8.4 mmol) was added dropwise to a solution of cobalt(II) chloride hexahydrate (1.00 g, 4.20 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (1.74 mL, 8.41 mmol) in 50% aqueous ethanol (12 mL). The resulting reaction mixture was stirred for 1 h. Distilled H_2O was added (23 mL) and, after 1 h, the resulting reaction mixture was poured through Büchner funnel and the filter cake washed with distilled H_2O (3 × 40 mL). The resulting solid was spread onto a watch glass and allowed to dry at ambient temperature for 18 h. $Co(thd)_2$ was isolated as a pink solid (1.18 g, 66%) and used without further purification.

Synthesis of Alcohols.

2-(4-Methoxyphenyl)pent-4-en-2-ol. To a solution of ketone **11** (0.500 g, 3.33 mmol) in THF (5.0 mL) at 0 °C was added a solution of allylmagnesium chloride in THF (2.0 M, 1.8 mL, 3.7 mmol) dropwise. The resulting reaction mixture was allowed to warm to room temperature over 30 min. Saturated aqueous NH_4Cl (5.0 mL) was added and the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. 2-(4-Methoxyphenyl)pent-4-en-2-ol was isolated as a colorless oil (0.607 g, 95%) and used without further purification. The spectroscopic data are consistent with the data reported:[50] ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 8.8, 2H), 6.88 (d, *J* = 8.7, 2H), 5.64 (m, 1H), 5.13 (m, 1H), 5.10 (s, 1H), 3.80 (s, 3H), 2.66 (dd, *J* = 13.5, 6.7, 1H), 2.49 (dd, *J* = 13.7, 8.3, 1H), 2.04 (s, 1H), 1.53 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) *δ* 158.5, 140.1, 134.1, 126.2, 119.5, 113.6, 73.5, 55.4, 48.7, 30.1.

2-Cyclohexylpent-4-en-2-ol. To a solution of acetylcyclohexane (0.436 mL, 3.17 mmol) in THF (4.7 mL) at 0 °C was added a solution of allylmagnesium chloride in THF (2.0 M, 1.7 mL, 3.5 mmol) dropwise. The resulting reaction mixture was allowed to warm to room temperature over 30 min. Saturated aqueous NH_4Cl (5.0 mL) was added and the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 90:10) afforded 2-cyclohexylpent-4-en-2-ol (0.389 g, 73%) as a yellow oil. The spectroscopic data are consistent with the data reported:[50] ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.89 (m, 1H), 5.18–5.07 (m, 2H), 2.23 (m, 2H), 1.87–1.64 (m, 5H), 1.39 (s, 1H), 1.36–1.13 (m, 4H), 1.09 (s, 3H), 1.06–0.93 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) *δ* 134.4, 118.8, 74.1, 47.7, 44.5, 27.8, 27.1, 26.97, 26.93, 26.8, 23.9.

2-(4-Methoxyphenyl)-3,3-dimethylpent-4-en-2-ol. To a solution of ketone **11** (0.300 g, 2.00 mmol) in THF (6.1 mL) at –78 °C was added a solution of prenylmagnesium chloride in THF (0.4 M, 5.5 mL, 2.2 mmol) dropwise. The resulting reaction mixture was allowed to warm to room temperature over 40 min. Saturated aqueous NH_4Cl (6.0 mL) was added and the mixture was extracted with diethyl ether (3 × 6 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 90:10) afforded 2-(4-methoxyphenyl)-3,3-dimethylpent-4-en-2-ol (0.324 g, 74%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.33 (d, *J* = 8.8, 2H), 6.84 (d, *J* = 8.8, 2H), 5.96 (dd, *J* = 17.6, 10.9, 1H), 5.13–5.00 (m, 2H), 3.81 (s, 3H), 1.88 (s, 1H), 1.56 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) *δ* 158.3 (C), 145.5 (CH), 137.8 (C), 128.4 (CH), 113.9 (CH_2), 112.6 (CH), 77.5 (C), 55.4 (CH_3), 44.7 (C), 25.7 (CH_3), 22.9 (CH_3), 22.6 (CH_3); IR (ATR) 3505, 2977, 1509, 1246, 1175, 1033, 830 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{20}NaO_2$ $(M + Na)^+$ 243.1356, found 243.1351.

2-(4-Methoxyphenyl)-4-methylpent-4-en-2-ol. To a solution of ketone **11** (0.300 g, 2.00 mmol) in THF (6.0 mL) at 0 °C was added a solution of 2-methylallylmagnesium chloride in THF (0.5 M, 4.4 mL, 2.2 mmol) dropwise. The resulting reaction mixture was allowed to warm to room temperature over 1 h. Saturated aqueous NH_4Cl (6.0 mL) was added and the mixture was extracted with diethyl ether (3 × 6 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 80:20) afforded 2-(4-methoxyphenyl)-4-methylpent-4-en-2-ol (0.270 g, 66%) as a colorless oil. The spectroscopic data are consistent with the data reported:[51] ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 8.8, 2H), 6.86 (d, *J* = 8.8, 2H), 4.89 (m, 1H), 4.74 (m 1H), 3.80 (s, 3H), 2.61 (d, *J* = 13.3, 1H), 2.49 (d, *J* = 13.4, 1H), 2.29 (s, 1H), 1.54 (s, 3H), 1.41 (s, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 142.9, 140.6, 126.1, 115.7, 113.5, 73.1, 55.4, 52.3, 30.9, 24.5.

Representative Procedure for the Silylation of Alcohols.

Diisopropyl((2-(4-methoxyphenyl)pent-4-en-2-yl)oxy)silane (**1**). To solution of 2-(4-methoxyphenyl)pent-4-en-2-ol (0.500 g, 2.60 mmol) and 1*H*-imidazole (0.354 g, 5.20 mmol) in THF (7.9 mL) was added diisopropylchlorosilane (0.488 mL, 2.86 mmol) dropwise. After 20 min, the reaction mixture was poured through a glass frit and the filter cake was washed with hexanes (3 × 8 mL). The filtrate was concentrated *in vacuo* and purification by flash chromatography (hexanes:EtOAc = 95:5) afforded diisopropylsilyl ether **1** (0.633 g, 79%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.9, 2H), 6.85 (d, J = 8.9, 2H), 5.62 (m, 1H), 4.97 (s, 1H), 4.94 (m, 1H), 4.34 (s, 1H), 3.81 (s, 3H), 2.56 (m, 2H), 1.62 (s, 3H), 1.08–0.88 (m, 14H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3 (C), 140.1 (C), 134.9 (CH), 126.8 (CH), 117.5 (CH_2), 113.2 (CH), 76.5 (C), 55.4 (CH_3), 50.4 (CH_2), 28.2 (CH_3), 18.1 (CH_3), 17.9 (CH_3), 17.83 (CH_3), 17.77 (CH_3), 13.6 (CH), 13.3 (CH); IR (ATR) 2941, 2864, 2097, 1512, 1248, 1001, 829, 805 cm^{-1}; Anal. Calcd. for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.87. Found: C, 70.83; H, 10.08.

Diisopropyl((2-phenylpent-4-en-2-yl)oxy)silane (**5**). Diisopropylsilyl ether **5** was prepared using the representative procedure for the silylation of alcohols using alcohol **7** (0.300 g, 1.85 mmol), 1*H*-imidazole (0.252 g, 3.70 mmol), and diisopropylchlorosilane (0.379 mL, 2.22 mmol) in THF (5.6 mL). The reaction time was 45 min. Purification by flash chromatography (hexanes:EtOAc = 95:5) afforded diisopropylsilyl ether **5** (0.273 g, 53%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.3, 2H), 7.22 (t, J = 7.3, 2H), 7.12 (t, J = 7.3, 1H), 5.53 (m, 1H), 4.89–4.82 (m, 2H), 4.29 (s, 1H), 2.49 (m, 2H), 1.56 (s, 3H), 1.02–0.83 (m, 14H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.9 (C), 134.7 (CH), 127.9 (CH), 126.7 (CH), 125.6 (CH), 117.6 (CH_2), 76.9 (C), 50.3 (CH_2), 28.3 (CH_3), 18.2 (CH_3), 17.9 (CH_3), 17.84 (CH_3), 17.76 (CH_3), 13.6 (CH), 13.3 (CH); IR (ATR) 2942, 2864, 2098, 1462, 1071, 999, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{26}NaSi$ $(M + Na - H_2O)^+$ 281.1696, found 281.1707.

Diisopropyl(((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)silane (**12**). Diisopropylsilyl ether **12** was prepared using the representative procedure for the silylation of alcohols using alcohol 1-(4-methoxyphenyl)but-3-en-1-ol (0.500 g, 2.81 mmol), 1*H*-imidazole (0.382 g, 5.61 mmol), and diisopropylchlorosilane (0.526 mL, 3.09 mmol) in THF (8.5 mL). The reaction time was 35 min. Purification by flash chromatography (hexanes:EtOAc = 95:5) afforded diisopropylsilyl ether **12** (0.525 g, 64%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.8, 2H), 6.85 (d, J = 8.8, 2H), 5.74 (m, 1H), 5.04–4.97 (m, 2H), 4.67 (t, J = 6.3, 1H), 4.14 (s, 1H), 3.80 (s, 3H), 2.53 (m, 1H), 2.42 (m, 1H), 1.07–0.87 (m, 14H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.9 (C), 136.6 (C), 135.2 (CH), 127.5 (CH), 117.2 (CH_2), 113.6 (CH), 76.9 (CH), 55.4 (CH_3), 45.1 (CH_2), 17.8 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.4 (CH_3), 12.8 (CH), 12.7 (CH); IR (ATR) 2941, 2864, 2091, 1512, 1246, 1000, 830, 798 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{27}O_2Si$ $(M + H - H_2O)^+$ 291.1775, found 291.1771. Anal. Calcd. for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.65. Found: C, 69.83; H, 9.71.

((2-Cyclohexylpent-4-en-2-yl)oxy)diisopropylsilane (**13**). Diisopropylsilyl ether **13** was prepared using the representative procedure for the silylation of alcohols using 2-cyclohexylpent-4-en-2-ol (0.389 g, 2.31 mmol), 1*H*-imidazole (0.314 g, 4.62 mmol), and diisopropylchlorosilane (0.434 mL, 2.54 mmol) in THF (7.0 mL). The reaction time was 1 h. Purification by flash chromatography (hexanes) afforded diisopropylsilyl ether **13** (0.505 g, 77%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (m, 1H), 5.04 (m, 2H), 4.35 (s, 1H), 2.33 (dd, J = 13.9, 7.3, 1H), 2.25 (dd, J = 13.9, 7.4, 1H), 1.83–1.63 (m, 5H), 1.32 (m, 1H), 1.17 (s, 3H), 1.17–0.85 (m, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.3 (CH), 117.1 (CH_2), 77.4 (C), 47.2 (CH_2), 44.9 (CH), 27.3 (CH_3), 27.2 (CH_3), 27.03 (CH_3), 27.02 (CH_3), 26.9 (CH_3), 24.8 (CH_2), 18.2 (CH_2), 18.1 (CH_2), 17.84 (CH_2), 17.82 (CH_2), 13.72 (CH), 13.67 (CH); IR (ATR) 2926, 2863, 2091, 1462, 1152, 1000, 814 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{34}KOSi$ $(M + K)^+$ 321.2011, found 321.2020. Anal. Calcd. for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.55; H, 12.33.

Diisopropyl((2-(4-methoxyphenyl)-4-methylpent-4-en-2-yl)oxy)silane (**14**). Diisopropylsilyl ether **14** was prepared using the representative procedure for the silylation of alcohols using 2-(4-methoxyphenyl)-4-methylpent-4-en-2-ol (0.268 g, 1.30 mmol), 1*H*-imidazole (0.177 g, 2.60 mmol), and diisopropylchlorosilane (0.244 mL, 1.43 mmol) in THF (3.9 mL). The reaction time was 35 min. Purification by flash chromatography (hexanes:EtOAc = 97:3) afforded diisopropylsilyl ether **14** (0.334 g, 80%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.9, 2H), 6.83 (d, J = 8.9, 2H), 4.74 (m, 1H), 4.56 (m, 1H), 4.27 (s, 1H), 3.80 (s, 3H), 2.56 (d, J = 13.4, 1H), 2.46 (d, J = 13.4, 1H), 1.67 (s, 3H), 1.45 (s, 3H), 1.09–0.86 (m, 14H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4 (C), 142.8 (C), 140.3 (C), 127.0 (CH), 114.9 (CH_2), 113.1 (CH), 76.9 (C), 55.4 (CH_3), 54.1 (CH_2), 28.0 (CH_3), 24.5 (CH_3), 18.1 (CH_3), 17.93 (CH_3), 17.87 (CH_3), 17.8 (CH_3), 13.5 (CH), 13.4 (CH); IR (ATR) 2941, 2864, 2099, 1611, 1511, 1248, 1097, 829 cm^{-1}. Anal. Calcd. for $C_{19}H_{32}O_2Si$: C, 71.19; H, 10.06. Found: C, 71.48; H, 10.32.

Diisopropyl((2-(4-methoxyphenyl)-3,3-dimethylpent-4-en-2-yl)oxy)silane (**15**). Diisopropylsilyl ether **15** was prepared using the representative procedure for the silylation of alcohols using 2-(4-methoxyphenyl)-3,3-dimethylpent-4-en-2-ol (0.320 g, 1.45 mmol), 1*H*-imidazole (0.396 g, 5.81 mmol), and diisopropylchlorosilane (0.546 mL, 3.20 mmol) in THF (4.4 mL). The reaction time was 18 h. Purification by flash chromatography (hexanes:EtOAc = 98:2) afforded diisopropylsilyl ether **15** (0.345 g, 71%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8, 2H), 6.79 (d, J = 8.8, 2H), 5.95 (dd, J = 17.8, 10.8, 1H), 4.92 (m, 2H), 4.26 (s, 1H), 3.81 (s, 3H), 1.63 (s, 3H), 1.15 (m, 6H), 1.01–0.84 (m, 14H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.2 (C), 146.0 (CH), 138.0 (C), 129.0 (CH), 112.2 (CH_2), 112.1 (CH), 80.8 (C), 55.3 (CH_3), 45.9 (C), 24.1 (CH_3), 22.9 (CH_3), 22.6 (CH_3), 18.4 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 13.8 (CH), 13.6 (CH); IR (ATR) 2942, 2864, 2098, 1510, 1248, 1097, 831, 807 cm^{-1}. Anal. Calcd. for $C_{20}H_{34}O_2Si$: C, 71.80; H, 10.24. Found: C, 71.54; H, 10.09.

Diisopropyl((((1R,2S*)-2-vinylcyclohexyl)oxy)silane* (**22**). Diisopropylsilyl ether **22** was prepared using the representative procedure for the silylation of alcohols using *trans*-2-vinylcyclohexan-1-ol (0.134 g, 1.06 mmol), 1*H*-imidazole (0.145 g, 2.12 mmol), and diisopropylchlorosilane (0.199 mL, 1.17 mmol) in THF (3.2 mL). The reaction time was 20 min. Purification by flash chromatography (hexanes:EtOAc = 99:1 → hexanes:EtOAc = 97:3) afforded diisopropylsilyl ether **22** (0.115 g, 45%) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (m, 1H), 5.00 (m, 2H), 4.18 (s, 1H), 3.34 (m, 1H), 1.97 (m, 2H), 1.74 (m, 2H), 1.63 (m, 1H), 1.33–1.84 (m, 4H), 1.03–0.94 (m, 14H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.0 (CH), 114.4 (CH_2), 77.2 (CH), 49.9 (CH), 35.3 (CH_2), 30.9 (CH_2), 25.2 (CH_2), 24.9 (CH_2), 17.81 (CH_3), 17.76 (CH_3), 17.73 (CH_3), 17.66 (CH_3), 12.9 (CH); IR (ATR) 2932, 2863, 2090, 1462, 1085, 1001, 907, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{27}Si$ $(M + H - H_2O)^+$ 223.1877, found 223.1880. Anal. Calcd. for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.67; H, 11.92.

(E)-Diisopropyl((3-methyloct-2-en-4-yl)oxy)silane (**25**). Diisopropylsilyl ether **25** was prepared using the representative procedure for the silylation of alcohols using (*E*)-3-methyloct-2-en-4-ol (0.394 g, 2.77 mmol), 1*H*-imidazole (0.378 g, 5.55 mmol), and diisopropylchlorosilane (0.521 mL, 3.05 mmol) in THF (8.4 mL).

The reaction time was 50 min. Purification by flash chromatography (pentanes) afforded diisopropylsilyl ether **25** (0.487 g, 68%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (q, J = 6.8, 1H), 4.09 (s, 1H), 3.95 (t, J = 6.8, 1H), 1.59 (d, J = 6.8, 3H), 1.57–1.43 (m, 5H), 1.34–1.12 (m, 4H), 1.05–0.93 (m, 14H), 0.88 (t, J = 7.2, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.7 (C), 120.5 (CH), 81.3 (CH), 35.7 (CH_2), 28.2 (CH_2), 22.9 (CH_2), 17.9 (CH_3), 17.70 (CH_3), 17.69 (CH_3), 17.5 (CH_3), 14.3 (CH_3), 13.1 (CH_3), 12.78 (CH), 12.77 (CH), 10.8 (CH_3); ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 12.0; IR (ATR) 2938, 2867, 1467, 903, 725 cm^{-1}. Anal. Calcd. for $C_{15}H_{32}OSi$: C, 70.24; H, 12.58. Found: C, 69.97; H, 12.40.

Diisopropyl((2-(4-methoxyphenyl)hex-5-en-2-yl)oxy)silane (**28**). Diisopropylsilyl ether **28** was prepared using the representative procedure for the silylation of alcohols using 2-(4-methoxyphenyl)hex-5-en-2-ol (0.230 g, 1.11 mmol), 1*H*-imidazole (0.152 g, 2.22 mmol), and diisopropylchlorosilane (0.209 mL, 1.22 mmol) in THF (3.4 mL). The reaction time was 40 min. Purification by flash chromatography (hexanes → hexanes:EtOAc = 99:1) afforded diisopropylsilyl ether **28** (0.225 g, 63%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8, 2H), 6.85 (d, J = 8.8, 2H), 5.73 (m, 1H), 4.90 (m, 2H), 4.63 (s, 1H), 3.81 (s, 3H), 2.01 (m, 1H), 1.86 (m, 2H), 1.77 (m, 1H), 1.63 (s, 3H), 1.12–0.92 (m, 14H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.0 (C), 140.0 (C), 139.1 (CH), 126.3 (CH), 113.9 (CH_2), 113.1 (CH), 76.7 (C), 55.2 (CH_3), 44.4 (CH_2), 29.4 (CH_3), 28.6 (CH_2), 18.0 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 13.4 (CH), 13.2 (CH); IR (ATR) 2942, 2097, 1611, 1509, 1462, 1247, 999, 907 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{33}O_2Si$ $(M + H)^+$ 321.2244, found 321.2245.

Representative Procedure for the Co-Catalyzed Silylperoxidation.

3,3-Diisopropyl-5-(4-methoxyphenyl)-5,7-dimethyl-1,2,4,3-trioxasilepane (**2**). A flask containing DCE (1,2-dichloroethane, 10 mL) was sparged with oxygen for 15 min. To a separate flask was added $Co(thd)_2$ (0.013 g, 0.032 mmol) followed by diisopropylsilyl ether **1** (0.097 g, 0.316 mmol). The oxygenated DCE (2.9 mL) was added to the reaction flask and the reaction vessel was sparged with oxygen for 2 min. A solution of *tert*-butyl hydroperoxide in CH_2Cl_2 (1.0 M, 0.016 mL, 0.016 mmol) was added followed by triethylsilane (0.051 mL, 0.316 mmol) and the reaction mixture was stirred at room temperature under a balloon of oxygen for 50 min. The reaction mixture was filtered through a 6-cm plug of silica, eluted with CH_2Cl_2 (45 mL), and concentrated *in vacuo*. Purification by flash chromatography using Brockmann grade III neutral alumina (pentanes:benzene = 80:20) afforded 3-sila-1,2,4-trioxepane **2** (0.046 g, 38%) as a colorless oil. Characterization was performed on an inseparable 67:33 mixture of diastereomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.9, 1.2H), 7.36 (d, J = 8.9, 2H), 6.88 (m, 3.2H), 4.60 (m, 0.5H), 3.96 (m, 1H), 3.81 (s, 1.8H), 3.80 (s, 3H), 2.50 (dd, J = 15.6, 10.4, 1H), 2.15 (dd, J = 15.4, 10.6, 0.6H), 2.09 (dd, J = 15.6, 3.4, 1H), 1.96 (dd, J = 15.4, 3.1, 0.6H), 1.72 (s, 1.8H), 1.54 (s, 3H), 1.28–1.25 (m, 6H), 1.20–1.17 (m, 3.4H), 1.14–1.09 (m, 18H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.33 (C), 158.27 (C), 142.6 (C), 139.4 (C), 126.2 (CH), 125.7 (CH), 113.6 (CH), 113.5 (CH), 79.4 (CH), 79.1 (CH), 78.4 (C), 55.49 (CH_3), 55.45 (CH_3), 46.7 (CH_2), 34.9 (CH_3), 28.3 (CH_3), 19.92 (CH_3), 19.88 (CH_3), 18.03 (CH_3), 17.97 (CH_3), 17.87 (CH_3), 17.71 (CH_3), 17.66 (CH_3), 17.59 (CH_3), 17.58 (CH_3), 17.51 (CH_3), 13.4 (CH), 13.2 (CH), 12.73 (CH), 12.68 (CH); IR (ATR) 2945, 2867, 1611, 1248, 1033, 907, 731 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{29}O_3Si$ $(M + H - H_2O)^+$ 321.1880, found 321.1891. Anal. Calcd. for $C_{18}H_{30}O_4Si$: C, 63.87; H, 8.93. Found: C, 63.95; H, 8.79.

3,3-Diisopropyl-5,7-dimethyl-5-phenyl-1,2,4,3-trioxasilepane (**6**). 3-Sila-1,2,4-trioxepane **6** was prepared using the representative procedure for the Co-catalyzed silylperoxidation using diisopropylsilyl ether **5** (0.072 g, 0.259 mmol), $Co(acac)_2$ (0.013 g, 0.052 mmol), *tert*-butyl hydroperoxide (0.013 mL, 0.013 mmol), and triethylsilane (0.082 mL, 0.518 mmol) in DCE (2.4 mL). The reaction time was 1.5 h. Purification by flash chromatography (pentanes:benzene = 80:20) afforded 3-sila-1,2,4-trioxepane **6** (0.017 g, 21%) as a colorless oil. Characterization was performed on an inseparable 59:41 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.41 (m, 3.5H), 7.34 (m, 3.4H), 7.23 (m, 1.5H), 4.63 (m, 0.7H), 3.94 (m, 1H), 2.53 (m, 1H), 2.15 (m, 1.6H), 1.99 (m, 0.7H), 1.75 (s, 1.8H), 1.57 (s, 3H), 1.28 (m, 6H), 1.22–1.08 (m, 22.9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.2 (C), 147.3 (C), 128.32 (CH), 128.27 (CH), 126.7 (CH), 126.6 (CH), 125.0 (CH), 124.5 (CH), 79.4 (CH), 79.1 (CH), 78.6 (C), 46.58 (CH_2), 34.9 (CH_3), 28.2 (CH_3), 19.9 (CH_3), 18.03 (CH_3), 17.98 (CH_3), 17.87 (CH_3), 17.7 (CH_3), 17.6 (CH_3), 17.5 (CH_3), 13.4 (CH), 13.2 (CH), 12.7 (CH); IR (ATR) 2944, 2867, 1464, 1121, 1035, 884, 699 cm^{-1}; HRMS (APCI) *m*/*z* calcd for $C_{16}H_{25}O_2Si$ $(M + H - H_2O)^+$ 277.1618, found 277.1631.

3,3-Diethyl-10-isopropyl-8-(4-methoxyphenyl)-6,8,11-trimethyl-4,5,9-trioxa-3,10-disiladodecane (**4**). Linear silyl peroxide **4** was prepared using the representative procedure for the Co-catalyzed silylperoxidation using diisopropylsilyl ether **4** (0.200 g, 0.653 mmol), $Co(thd)_2$ (0.028 g, 0.065 mmol), *tert*-butyl hydroperoxide (0.033 mL, 0.033 mmol), and triethylsilane (1.04 mL, 6.53 mmol) in DCE (3.0 mL). The reaction time was 2 h. Purification by flash chromatography using Brockmann grade III neutral alumina (pentanes:benzene = 80:20), then silica gel (hexanes:EtOAc = 97:3) yielded linear silyl peroxide **4** as a colorless oil (0.086 g, 29%). Characterization was performed on an inseparable 67:33 mixture of diastereomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J = 8.8, 3.5H), 6.84 (m, 3.5H), 4.34 (s, 1H), 4.30 (0.5H), 4.19 (m, 0.5H), 3.80 (s, 4.5H), 3.75 (m, 1H), 2.26 (dd, J = 14.3, 5.1, 1H), 2.17 (dd, J = 14.4, 4.4, 0.5H), 1.86 (dd, J = 14.3, 5.7, 1H), 1.82 (dd, J = 14.3, 6.2, 0.5H), 1.69 (s, 1.5H), 1.68 (s, 3H), 1.10–1.04 (m, 14.3H), 1.00–0.90 (m, 30.5H), 0.63 (m, 3.6H), 0.57 (m, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.42 (C), 158.40 (C), 140.6 (C), 139.5 (C), 126.9 (CH), 126.7 (CH), 113.3 (CH), 78.9 (CH), 78.6 (CH), 76.5 (C), 75.9 (C), 55.4 (CH_3), 50.6 (CH_2), 50.1 (CH_2), 29.8 (CH_3), 28.6 (CH_3), 20.19 (CH_3), 20.16 (CH_3), 18.1 (CH_3), 17.94 (CH_3), 17.90 (CH_3), 17.86 (CH_3), 13.54 (CH_3), 13.50 (CH_3), 13.4 (CH_3), 13.3 (CH_3), 7.0 (CH_3), 6.9 (CH_3), 4.0 (CH_2), 3.9 (CH_2); IR (ATR) 2954, 2099, 1510, 1248, 906, 729 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{45}O_3Si_2$ $(M + H - H_2O)^+$ 437.2902, found 437.2907.

4-((Diisopropyl(1-phenylethoxy)silyl)peroxy)-2-phenylpentan-2-ol (**9** and **10**). Linear silyl peroxides **9** and **10** were prepared using the representative procedure for the Co-catalyzed silylperoxidation using alcohol **7** (0.050 g, 0.308 mmol), $Co(thd)_2$ (0.013 g, 0.031 mmol), *tert*-butyl hydroperoxide (0.015 mL, 0.015 mmol), and diisopropylsilane **8** (0.146 g, 0.616 mmol) in DCE (2.8 mL). The reaction time was 19 h. Purification by flash chromatography using Brockmann grade III neutral alumina (hexanes:EtOAc = 97:3) yielded linear silyl peroxide **9** a colorless oil (0.015 g, 11%) and linear silyl peroxide **10** as a colorless oil (0.009 g, 7%). **Linear Silyl Peroxide 9:** Characterization was performed on an inseparable 53:47 mixture of diastereomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (m, 4H), 7.36–7.27 (m, 12H), 7.25–7.20 (m, 4H), 5.05 (q, J = 6.4, 1H), 5.02 (q, J = 6.4, 0.9H), 4.17 (s, 0.9H), 4.13 (s, 1H), 3.93 (m, 1H), 3.86 (m, 0.8H), 2.21–2.08 (m, 4H), 1.48 (m, 6H), 1.44 (m, 6H), 1.14–0.88 (m, 36.4H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.09 (C), 148.07 (C), 146.41 (C), 146.36 (C), 128.4 (CH), 128.29 (CH), 128.28 (CH), 127.04 (CH), 127.01 (CH), 126.5 (CH), 125.4 (CH), 125.3 (CH), 125.22 (CH), 125.21 (CH), 80.2 (CH), 80.1 (CH), 73.89 (C), 73.86 (C), 71.5 (CH), 71.4 (CH), 49.4 (CH_2), 49.3 (CH_2), 32.6 (CH_3), 27.43 (CH_3), 27.42 (CH_3), 20.11 (CH_3), 20.06 (CH_3), 17.61 (CH_3), 17.56 (CH_3), 17.54 (CH_3), 17.51 (CH_3), 17.50 (CH_3), 17.4 (CH_3), 11.90 (CH), 11.85 (CH), 11.75 (CH); IR (ATR) 3466, 2868, 1493, 906, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd for

$C_{25}H_{40}NO_3Si$ $(M + NH_4 - H_2O)^+$ 430.2772, found 430.2774. **Linear Silyl Peroxide 10:** Characterization was performed on a 50:50 mixture of diastereomers: ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 (m, 3.8H), 7.39–7.29 (m, 11.6H), 7.22 (m, 3.8H), 5.11 (q, J = 6.3, 2H), 4.29 (m, 2H), 3.28 (s, 0.9H), 3.25 (s, 0.9H), 2.17 (m, 2H), 1.86 (m, 1.9H), 1.58 (s, 5.4H), 1.48 (m, 5.4H), 1.16–0.92 (m, 32.4H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.8 (C), 146.5 (C), 128.3 (CH), 127.1 (CH), 126.7 (CH), 125.4 (CH), 124.9 (CH), 79.7 (CH), 73.4 (C), 71.4 (CH), 49.6 (CH_2), 29.8 (CH_3), 27.5 (CH_3), 20.1 (CH_3), 17.6 (CH_3), 17.4 (CH_3), 11.9 (CH), 11.8 (CH); IR (ATR) 3476, 2867, 1447, 1371, 1095, 907, 731, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{38}NaO_4Si$ $(M + Na)^+$ 453.2432, found 453.2433.

3,3-Diethyl-11-isopropyl-9-(4-methoxyphenyl)-6,9,12-trimethyl-4,5,10-trioxa-3,11-disilatridecane (**29**). Linear silyl peroxide **29** was prepared using the representative procedure for the Co-catalyzed silylperoxidation using diisopropylsilyl ether **28** (0.040 g, 0.155 mmol), $Co(thd)_2$ (0.007 g, 0.016 mmol), *tert*-butyl hydroperoxide (0.008 mL, 0.008 mmol), and triethylsilane (0.025 mL, 0.156 mmol) in DCE (1.4 mL). The reaction time was 20 min. Purification by flash chromatography using Brockmann grade III neutral alumina (pentane → hexanes:EtOAc = 98:2) yielded linear silyl peroxide **29** as a colorless oil (0.028 g, 48%). Characterization was performed on an inseparable 50:50 mixture of diastereomers: ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.9, 4H), 6.84 (d, J = 8.9, 4H), 4.36 (s, 1.9H), 3.89 (m, 2H), 3.80 (s, 6H), 1.90 (m, 2H), 1.78 (m, 2H), 1.61 (s, 6H), 1.35 (m, 2H), 1.13–0.93 (m, 54H), 0.66 (q, J = 7.9, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.2 (C), 140.2 (C), 140.1 (C), 126.57 (CH), 126.56 (CH), 113.1 (CH), 81.8 (CH), 81.7 (CH), 76.9 (C), 55.4 (CH_3), 41.2 (CH_2), 41.0 (CH_2), 29.9 (CH_3), 29.8 (CH_3), 29.5 (CH_2), 29.3 (CH_2), 18.7 (CH_3), 18.6 (CH_3), 18.17 (CH_3), 18.16 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.83 (CH_3), 17.80 (CH_3), 13.7 (CH), 13.6 (CH), 13.37 (CH), 13.35 (CH), 6.9 (CH_3), 4.0 (CH_2); IR (ATR) 2953, 2097, 1510, 1246, 906, 729 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{45}O_3Si_2$ $(M + H - H_2O)^+$ 437.2902, found 437.2907.

Representative Procedure for the Co-Catalyzed Synthesis of Diisopropylsilylene Acetals.

2,2-Diisopropyl-4-(4-methoxyphenyl)-4,6-dimethyl-1,3,2-dioxasilinane (**3**). A flask containing DCE (1,2-dichloroethane, 10 mL) was sparged with oxygen for 15 min. To a separate flask was added $Co(thd)_2$ (0.043 g, 0.100 mmol) followed by diisopropylsilyl ether **1** (0.306 g, 1.00 mmol). The oxygenated DCE (9.1 mL) was added to the reaction flask and the reaction vessel was sparged with oxygen for 2 min. A solution of *tert*-butyl hydroperoxide in CH_2Cl_2 (1.0 M, 0.050 mL, 0.050 mmol) was added followed by triethylsilane (0.160 mL, 1.00 mmol) and the reaction mixture was stirred at room temperature under a balloon of oxygen for 30 min. The reaction mixture was filtered through a 6-cm plug of silica, eluted with CH_2Cl_2 (45 mL), and concentrated *in vacuo*. To the crude reaction mixture was added toluene (2.0 mL) and triphenylphosphine (0.524 g, 2.00 mmol). The reaction mixture was stirred at 40 °C for 3 h. Hydrogen peroxide (27% w/w aqueous solution, 1.0 mL, 8.7 mmol) was added and the resulting reaction mixture was stirred at room temperature for 15 min. The reaction mixture was diluted with hexanes (9.1 mL) and poured through a glass frit. The filter cake was washed with hexanes (3 × 9 mL). The filtrate was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography using Brockmann grade III neutral alumina (pentanes:benzene = 80:20) afforded diisopropylsilylene acetal **3** (0.192 g, 60%) as a colorless oil. Characterization was performed on an inseparable 51:49 mixture of diastereomers: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8, 3.8H), 6.87 (d, J = 8.8, 3.8H), 4.44 (m, 1H), 3.92 (m, 1H), 3.83 (s, 2.5H), 3.80 (s, 3H), 2.30 (dd, J =14.7, 1.2, 0.9H), 1.90 (dd, J = 14.4, 2.0, 1H), 1.87 (dd, J = 14.8, 10.9, 0.9H), 1.75 (dd, J = 14.6, 11.3, 1H), 1.59 (s, 3H), 1.46 (s, 2.5H), 1.24 (d, J = 6.1, 3H), 1.18 (d, J = 6.2, 2.7H), 1.11–0.91 (m, 27.5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3 (C), 158.2 (C), 142.9 (C), 140.0 (C), 126.6 (CH), 125.4 (CH), 113.52 (CH), 113.46 (CH), 76.6 (C), 75.3 (C), 66.3 (CH), 66.2 (CH), 55.5 (CH_3), 55.4 (CH_3), 50.0 (CH_2), 48.9 (CH_2), 35.7 (CH_3), 29.9 (CH_3), 25.0 (CH_3), 24.8 (CH_3), 17.6 (CH_3), 17.4 (CH_3), 17.32 (CH_3), 17.26 (CH_3), 17.23 (CH_3), 17.18 (CH_3), 17.12 (CH_3), 17.11 (CH_3), 14.2 (CH_2), 13.9 (CH_2), 13.41 (CH_2), 13.38 (CH_2); IR (ATR) 2943, 2865, 1611, 1511, 1248, 983 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{34}NO_3Si$ $(M + NH_4)^+$ 340.2302, found 340.2308. Anal. Calcd. for $C_{18}H_{30}O_3Si$: C, 67.03; H, 9.38. Found: C, 67.33; H, 9.46.

Diisopropylsilylene Acetal 3 Prepared Using Catalytic Phenylsilane. Diisopropylsilylene acetal **3** was prepared using the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **1** (0.165 g, 0.539 mmol), $Co(thd)_2$ (0.034 g, 0.081 mmol), *tert*-butyl hydroperoxide (0.027 mL, 0.027 mmol), and a solution of phenylsilane in $PhCF_3$ (0.20 M, 0.54 mL, 0.11 mmol) in DCE (4.9 mL). The reaction time was 15 min. Reduction of the peroxide unit was performed using toluene (1.0 mL) and triphenylphosphine (0.283 g, 1.08 mmol). The reaction time was 1 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 0.54 mL, 4.7 mmol). The reaction time was 15 min. Purification by flash chromatography using Brockmann grade III neutral alumina (hexanes → hexanes:EtOAc = 95:5) afforded diisopropylsilylene acetal **3** (0.126 g, 73%) as a colorless oil. Characterization was performed on an inseparable 50:50 mixture of diastereomers. The spectroscopic data are consistent with the data reported above for diisopropylsilylene acetal **3**.

2,2-Diisopropyl-4-(4-methoxyphenyl)-6-methyl-1,3,2-dioxasilinane (**16**) and *1-(4-methoxyphenyl)butane-1,3-diol* (**20**). Diisopropylsilylene acetal **16** and 1,3-diol **20** were prepared using the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **12** (0.292 g, 1.00 mmol), $Co(thd)_2$ (0.043 g, 0.100 mmol), *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol), and triethylsilane (0.160 mL, 1.00 mmol) in DCE (9.1 mL). The reaction mixture was heated to 40 °C for 1 h. Reduction of the peroxide unit was performed using toluene (2.0 mL) and triphenylphosphine (0.524 g, 2.00 mmol). The reaction time was 2 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 1.0 mL, 8.7 mmol). Purification by flash chromatography using Brockmann grade III neutral alumina (pentanes:benzene = 95:5 → hexanes:EtOAc 50:50 → hexanes:EtOAc 40:60) afforded diisopropylsilylene acetal **16** (0.047 g, 15%) as a colorless oil and 1,3-diol **20** (0.041 g, 21%) as a colorless oil. **Diisopropylsilylene Acetal 16**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.7, 2H), 6.89 (d, J = 8.7, 2H), 5.07 (dd, J = 11.3, 2.1, 1H), 4.36 (m, 1H), 3.81 (s, 3H), 1.83 (m, 1H), 1.63 (m, 1H), 1.25 (d, J = 6.3, 3H), 1.13–1.03 (m, 14H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.0 (C), 137.4 (C), 126.5 (CH), 113.9 (CH), 75.4 (CH), 70.3 (CH), 55.5 (CH_3), 47.6 (CH_2), 24.9 (CH_3), 17.34 (CH_3), 17.31 (CH_3), 17.03 (CH_3), 17.00 (CH_3), 14.0 (CH), 12.4 (CH); IR (ATR) 2864, 1613, 1513, 1245, 1136, 980, 892 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{27}O_2Si$ $(M + H - H_2O)^+$ 291.1775, found 291.1771. **1,3-Diol 20:** Characterization was performed on an inseparable 67:33 mixture of diastereomers: ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2.9H), 6.87 (m, 2.9H), 4.98 (m, 1H), 4.86 (0.5H), 4.07 (m, 1.5H), 3.79 (m, 4.3H), 3.31 (s, 0.5H), 3.28 (s, 0.5H), 3.06 (s, 1H), 2.58 (s, 1H), 1.91–1.69 (m, 3H), 1.21 (m, 4.4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.3 (C), 159.1 (C), 136.9 (C), 136.8 (C), 127.1 (CH), 127.0 (CH), 114.1 (CH), 114.0 (CH), 75.1 (CH), 71.6 (CH), 68.9 (CH), 65.6 (CH), 55.5 (CH_3), 47.2 (CH_2), 46.3 (CH_2), 24.3 (CH_3), 23.4 (CH_3); IR (ATR) 3348, 2966, 1611, 1512, 1244, 904, 726, 648 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{16}NaO_3$ $(M + Na)^+$ 219.0992, found 219.1001.

4-Cyclohexyl-2,2-diisopropyl-4,6-dimethyl-1,3,2-dioxasilinane (**17**). Diisopropylsilylene acetal **17** was prepared using the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **13** (0.282 g, 1.00 mmol), $Co(acac)_2$ (0.103 g, 0.400 mmol), *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol), and triethylsilane (0.319 mL, 2.00 mmol) in DCE (9.1 mL). The reaction mixture was heated to 40 °C for 2 h. Reduction of the peroxide unit was performed using toluene (2.0 mL) and triphenylphosphine (0.524 g, 2.00 mmol). The reaction time was 1 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 1.0 mL, 8.7 mmol). Purification by flash chromatography (pentanes:benzene = 95:5 → pentanes:benzene = 80:20) afforded diisopropylsilylene acetal **17** (0.184 g, 62%) as a colorless oil. Characterization was performed on an inseparable 51:49 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (m, 1.9H), 2.09 (m, 1H), 1.97–1.40 (m, 14.3H), 1.37–1.08 (m, 16.8H), 1.06 (s, 3H), 1.05–0.84 (m, 30.9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 76.5 (C), 76.1 (C), 65.9 (CH), 65.3 (CH), 51.7 (CH), 46.4 (CH), 45.98 (CH), 45.97 (CH_2), 29.3 (CH_2), 27.8 (CH_2), 27.2 (CH_2), 27.1 (CH_2), 27.02 (CH_2), 26.96 (CH_2), 26.91 (CH_2), 26.89 (CH_2), 26.88 (CH_2), 25.3 (CH_3), 25.23 (CH_3), 25.16 (CH_3), 23.3 (CH_3), 17.5 (CH_3), 17.4 (CH_3), 17.33 (CH_3), 17.28 (CH_3), 17.25 (CH_3), 17.0 (CH_3), 14.0 (CH), 13.9 (CH), 13.5 (CH), 13.3 (CH); IR (ATR) 2927, 2864, 1464, 1148, 980, 882 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{33}OSi$ $(M + H - H_2O)^+$ 281.2295, found 281.2303.

2,2-Diisopropyl-4-(4-methoxyphenyl)-4,6,6-trimethyl-1,3,2-dioxasilinane (**18**). Diisopropylsilylene acetal **18** was prepared using the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **14** (0.320 g, 1.00 mmol), $Co(acac)_2$ (0.103 g, 0.400 mmol), *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol), and triethylsilane (0.319 mL, 2.00 mmol) in DCE (9.1 mL). The reaction mixture was heated to 40 °C for 3 h. Reduction of the peroxide unit was performed using toluene (2.0 mL) and triphenylphosphine (0.524 g, 2.00 mmol). The reaction time was 2.5 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 1.0 mL, 8.7 mmol). Purification by flash chromatography (pentanes:benzene = 80:20) afforded diisopropylsilylene acetal **18** (0.130 g, 39%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8, 2H), 6.85 (d, J = 8.8, 2H), 3.80 (s, 3H), 2.30 (d, J = 14.9, 1H), 2.12 (d, J = 14.9, 1H), 1.49 (s, 3H), 1.30 (s, 3H), 1.12–0.96 (m, 14H), 0.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1 (C), 142.2 (C), 125.7 (CH), 113.4 (CH), 75.8 (C), 72.6 (C), 55.4 (CH_3), 51.6 (CH_2), 36.3 (CH_3), 33.5 (CH_3), 30.8 (CH_3), 17.7 (CH_3), 17.60 (CH_3), 17.57 (CH_3), 17.4 (CH_3), 14.3 (CH), 14.2 (CH); IR (ATR) 2967, 2865, 1611, 1510, 1243, 1036, 992 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{19}H_{32}NaO_3Si$ $(M + Na)^+$ 359.2013, found 359.2017. Anal. Calcd. for $C_{19}H_{32}O_3Si$: C, 67.81; H, 9.58. Found: C, 68.07; H, 9.72.

2,2-Diisopropyl-4-(4-methoxyphenyl)-4,5,5,6-tetramethyl-1,3,2-dioxasilinane (**19**). Diisopropylsilylene acetal **19** was prepared using the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **15** (0.290 g, 0.867 mmol), $Co(acac)_2$ (0.089 g, 0.347 mmol), *tert*-butyl hydroperoxide (0.043 mL, 0.043 mmol), and triethylsilane (0.277 mL, 1.73 mmol) in DCE (7.9 mL). The reaction mixture was heated to 40 °C for 5 h. Reduction of the peroxide unit was performed using toluene (1.7 mL) and triphenylphosphine (0.455 g, 1.73 mmol). The reaction time was 45 min. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 0.87 mL, 7.6 mmol). Purification by flash chromatography (pentanes:benzene = 80:20) afforded diisopropylsilylene acetal **19** (0.098 g, 32%) as a colorless oil. Characterization was performed on an inseparable 70:30 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.36 (m, 2.8H), 6.89–6.83 (m, 2.8H), 4.43 (q, J = 6.3, 1H), 4.11 (q, J = 6.7, 0.4H), 3.81 (m, 4.1H), 1.71 (s, 3H), 1.66 (s, 1.3H), 1.29–1.03 (m, 27H), 0.79 (s, 3H), 0.68 (s. 3H), 0.59 (s, 1.3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.24 (C), 158.16 (C), 139.7 (C), 138.5 (C), 128.7 (CH), 128.4 (CH), 112.51 (CH), 112.50 (CH), 83.3 (C), 82.5 (C), 73.6 (CH), 72.5 (CH), 55.40 (CH_3), 55.39 (CH_3), 43.7 (C), 43.6 (C), 27.4 (CH_3), 25.9 (CH_3), 24.8 (CH_3), 22.4 (CH_3), 19.5 (CH_3), 19.1 (CH_3), 18.2 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 17.73 (CH_3), 17.68 (CH_3), 17.66 (CH_3), 16.1 (CH_3), 15.1 (CH), 15.0 (CH), 14.7 (CH), 13.5 (CH); IR (ATR) 2944, 2865, 1610, 1510, 1245, 1118, 1036, 825, 684 cm^{-1}. Anal. Calcd. for $C_{20}H_{34}O_3Si$: C, 68.52; H, 9.78. Found: C, 68.80; H, 9.86.

2-Cyclohexylpentane-2,4-diol (**21**). 1,3-Diol **21** was prepared using a modification of the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **13** (0.282 g, 1.00 mmol), $Co(thd)_2$ (0.043 g, 0.100 mmol), *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol), and triethylsilane (0.160 mL, 1.00 mmol) in DCE (9.1 mL). The reaction time was 1 h. Reduction of the peroxide unit was performed using toluene (2.0 mL) and triphenylphosphine (0.524 g, 2.00 mmol). The reaction time was 1 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 1.0 mL, 8.7 mmol).

To unpurified diisopropylsilylene acetal **17** was added THF (5.0 mL) followed by a solution of tetrabutylammonium fluoride in THF (1.0 M, 2.4 mL, 2.4 mmol). The reaction mixture was stirred for 1 h. Distilled H_2O (5.0 mL) was added, then the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc 70:30 → hexanes:EtOAc 65:35) afforded 1,3-diol **21** (0.147 g, 79%) as a colorless oil. Characterization was performed on an inseparable 50:50 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (m, 2H), 1.96–1.43 (m, 16H), 1.32–0.92 (m, 24H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 76.1 (C), 75.9 (C), 65.6 (CH), 65.2 (CH), 50.7 (CH), 47.2 (CH_2), 45.5 (CH), 45.2 (CH_2), 29.0 (CH_2), 27.5 (CH_2), 27.14 (CH_2), 26.97 (CH_2), 26.92 (CH_2), 26.91 (CH_2), 26.89 (CH_2), 26.79 (CH_2), 26.76 (CH_2), 26.74 (CH_2), 25.0 (CH_3), 24.7 (CH_3), 24.6 (CH_3), 23.6 (CH_3); IR (ATR) 3329, 2924, 2852, 1450, 1136, 1076 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{22}NaO_2$ $(M + Na)^+$ 209.1512, found 209.1502.

(1R,2S*)-2-((R*)-1-Hydroxyethyl)cyclohexan-1-ol* (**24**). 1,3-Diol **24** was prepared using a modification of the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **22** (0.145 g, 0.596 mmol), $Co(thd)_2$ (0.025 g, 0.060 mmol), *tert*-butyl hydroperoxide (0.030 mL, 0.030 mmol), and triethylsilane (0.091 mL, 0.596 mmol) in DCE (5.4 mL). The reaction time was 1 h. Reduction of the peroxide unit was performed using toluene (1.2 mL) and triphenylphosphine (0.312 g, 1.19 mmol). The reaction time was 2.5 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 0.60 mL, 5.2 mmol).

To unpurified diisopropylsilylene acetal **23** was added THF (3.0 mL) followed by a solution of tetrabutylammonium fluoride in THF (1.0 M, 1.4 mL, 1.4 mmol). The reaction time was for 30 min. Distilled H_2O (3.0 mL) was added then, the mixture was extracted with diethyl ether (3 × 3 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 50:50) afforded 1,3-diol **24** (0.062 g, 73%) as a colorless oil. Characterization was performed on an inseparable 57:43 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (m, 1H), 3.79 (s, 1H), 3.68 (m, 0.8H), 3.58 (m, 1H), 3.44 (m, 0.8H), 3.19 (s, 1H), 3.00 (s, 1H), 1.87 (m, 2H), 1.66–1.44 (m, 6.2H), 1.26–1.03 (m, 11H), 0.94–0.68 (m, 1.8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 76.7 (CH), 74.3 (CH), 71.8

(CH), 71.4 (CH), 50.9 (CH), 49.9 (CH), 35.9 (CH_2), 35.8 (CH_2), 27.6 (CH_2), 27.3 (CH_2), 25.8 (CH_2), 25.5 (CH_2), 24.9 (CH_2), 24.7 (CH_2), 21.9 (CH_3), 18.4 (CH_3); IR (ATR) 3329, 2930, 2857, 1449, 1035, 907 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_8H_{18}NO$ ($M + NH_4 - H_2O)^+$ 144.1383, found 144.1388.

3-Methyloctane-3,4-diol (**27**). 1,2-Diol **27** was prepared using a modification of the representative procedure for the Co-catalyzed synthesis of diisopropylsilylene acetals using diisopropylsilyl ether **25** (0.257 g, 1.00 mmol), $Co(thd)_2$ (0.085 g, 0.200 mmol), *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol), and triethylsilane (0.160 mL, 1.00 mmol) in DCE (9.1 mL). The reaction time was 1.5 h. Reduction of the peroxide unit was performed using toluene (2.0 mL) and triphenylphosphine (0.524 g, 2.00 mmol). The reaction time was 4 h. Oxidation of the remaining triphenylphosphine was performed using hydrogen peroxide (27% w/w aqueous solution, 1.0 mL, 8.7 mmol). Characterization was performed on an analytical sample of diisopropylsilylene acetal **26**: ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ 15.4.

To unpurified diisopropylsilylene acetal **26** was added THF (5.0 mL) followed by a solution of tetrabutylammonium fluoride in THF (1.0 M, 2.4 mL, 2.4 mmol). The reaction mixture was stirred for 10 min. Distilled H_2O (5.0 mL) was added, then the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (hexanes = hexanes:EtOAc = 80:20) afforded 1,2-diol **27** (0.030 g, 19%) as a colorless oil. Characterization was performed on an inseparable 56:44 mixture of diastereomers: ^1H NMR (400 MHz, $CDCl_3$) δ 3.39 (m, 1.8H), 2.22 (s, 1H), 2.12 (s, 0.8H), 2.02–1.87 (m, 1.8H), 1.79 (s, 0.8H), 1.67–1.27 (m, 15H), 1.13 (s, 2.3H), 1.07 (s, 3H), 0.95–0.88 (m, 10.7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 78.6 (CH), 77.0 (CH), 75.2 (C), 75.0 (C), 31.7 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 23.1 (CH_3), 22.92 (CH_2), 22.91 (CH_2), 20.6 (CH_3), 14.2 (CH_3), 7.79 (CH_3), 7.75 (CH_3); IR (ATR) 3393, 2957, 1461, 1378, 996, 907, 732 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_{23}NO$ ($M + NH_4 - H_2O)^+$ 161.1774, found 161.1778.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Spectral data (PDF)

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Notes

The authors declare no competing financial interests.

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