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The Photolytic and Hydrolytic Lability of Sisyl ($Si(SiMe_3)_3$) Ethers, An Alcohol Protecting Group

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Summary: The tris(trimethylsilyl)silyl (sisyl) group is a photolabile protecting group for primary and secondary alcohols. Sisyl (tris(trimethylsilyl)silyl) ethers **2b-11b** of a number of primary and secondary alcohols **2a-11a** were prepared in yields ranging from 70-97%. The resulting silyl ethers were stable to aqueous bases, Grignard reagents and Wittig reagents as would be expected for bulky alkoxysilanes. They were also stable to selected fluoride salts including CsF. The sisyl ethers could be cleaved using photolysis at 254 nm in under 30 minutes to give the starting alcohols in yields ranging from 62-95%. The photolytic behaviour of sisyl ethers was examined in more detail using 2,3-dimethyl-1,3-butadiene as a silylene trap. The regiochemistry of the oligosilane fragmentation to silylenes was shown to be dependent upon the alkoxy group. The hydrolytic stability of three sisyl ethers was compared with the analogous *t*-butyldimethylsilyl ethers. The relative stability of the two silyl groups can be altered by choice of solvent: in acetic acid/water the ease of hydrolysis followed the order $ROSi(SiMe_3)_3$ > $ROSiMe_2t$-Bu; the inverse order was observed in $CDCl_3$ using *p*-$TsOH{\cdot}H_2O$. Pseudo-first-order rate constants for the acidic hydrolysis of primary, benzylic, and secondary sisyl ethers in $AcOH/THF/H_2O$ were determined to be 3.74×10^{-2} s^{-1}, 1.94×10^{-2} s^{-1}, and 1.30×10^{-2} s^{-1}, respectively. The analogous rate constants for the TBS ethers were determined to be 6.04×10^{-3} s^{-1}, 3.53×10^{-3} s^{-1}, and 3.49×10^{-3} s^{-1}, respectively.

Keywords: Hydrolysis; Kinetics; Photochemistry; Protecting groups; Silicon and compounds

INTRODUCTION

The "gold standard" for the protection of alcohols is the silyl ether.[2,3] One enormous advantage associated with the use of silyl ethers is the ability to regenerate the alcohols using fluoride under conditions that do not generally affect the rest of the molecule. In addition, the steric bulk of the ligands on silicon can be reliably used to control the ease of preparation and deprotection of silyl ethers.[4] Thus, as the size of the group

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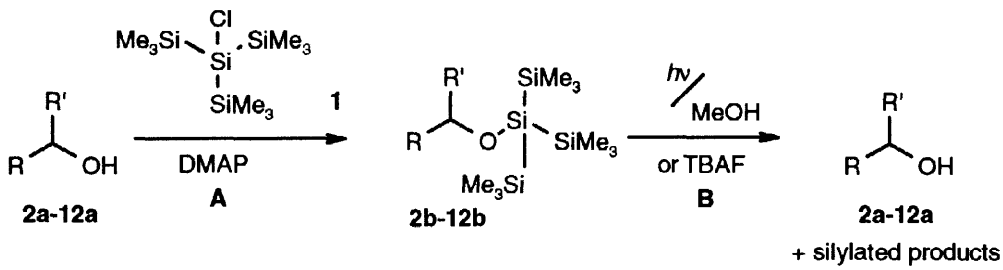
increases from trimethylsilyl[5] to *t*-butyldimethylsilyl,[6,7] *t*-butyldiphenylsilyl[8] and triisopropylsilyl,[9] for instance, it is increasingly difficult to introduce the silyl group and to effect deprotection via acidic or basic hydrolysis.[2,10]

Frequently, in synthetic operations, it is important to be able to selectively remove protecting groups. Thus, there is a need for methods that override the general trends for hydrolysis rates based on steric bulk. The photolytic cleavage of silyl ethers provides an alternative approach to selective deprotection that does not rely on steric bulk for discrimination between silyl groups, and which has received little attention.[11] We have previously reported on the use of tris(trimethylsilyl)silyl (sisyl) ethers as photolabile protecting groups.[12] One focus of this manuscript is to examine the reaction conditions to which sisyl ethers are stable. The other major focus is an examination of the mechanisms by which sisyl ethers may be excised from organic molecules. We have investigated the decomposition using photolysis and, additionally, compared the hydrolytic stability of sisyl ethers with the workhorse protecting group, the *t*-butyldimethylsilyl group (TBS).

RESULTS AND DISCUSSION

Tris(trimethylsilyl)silyl ethers were prepared by the simple and traditional expedient of reacting the chlorosilane with an alcohol in the presence of 4-dimethylaminopyridine (DMAP): TBS ethers were prepared in an analogous manner from *t*-butylchlorodimethylsilane. CH_2Cl_2 was chosen as solvent over DMF[7] both because of the excellent solubility of the alcohols examined in this solvent and its efficient removal at the end of the reaction (Scheme 1A). Sisyl chloride **1** is simply formed from tris(trimethylsilyl)silane by stirring with carbon tetrachloride.[13]

A number of different alcohols were protected using **1**. The reaction between primary or secondary alcohols and the sisyl chloride in CH_2Cl_2 took place at room temperature to give yields of sisyl ethers of 70-97% after purification (**2a-12a** → **2b-12b**, Scheme 1, Table 1). Although tertiary or bulky secondary alcohols could not be converted to sisyl ethers in good yield, this problem is common for bulky silyl ethers: the corresponding *t*-butyldimethylsilyl ethers are generally prepared from the more reactive *t*-butyldimethylsilyl triflate, rather than the chloride[14].



Scheme 1

Stability to Synthetic Reagents: The utility of a protecting group is clearly related to its resistance to a variety of conditions routinely used in organic synthesis. It was possible to show that sisyl ethers are not stable towards *n*-BuLi, to $LiAlH_4$ or, presumably, to related nucleophiles. In both cases, a mixture of products including the unprotected alcohol was recovered. Likely, the external $SiMe_3$ group is vulnerable to attack by such strong nucleophiles.[15] However, sisyl ethers were stable[16] to related, less reactive organometallic reagents

(3.0 M MeMgBr; $Ph_3P{=}CH_2$) and were also stable towards oxidation (Jones reagent). The question of stability to acid is addressed below.

Table 1: Alcohols Protected with Chlorotris(trimethylsilyl)silane and Silyl Ether Deprotection

Compound	Alcohol	Protection[a] (% Yield 2-12b)	Deprotection[a] (% Yield 2-11a)
Geraniol	**2**	74	90
Decanol	**3**	85	68
2-Octanol	**4**	78	95
Cyclopentanol	**5**	70	88
Cholesterol	**6**	79	87[b]
2,2,2-Trifluoroethanol	**7**	97	62[c]
2-Chloroethanol	**8**	89	90
2,2,2-Trichloroethanol	**9**	83	89
2-Phenylethanol	**10**	85	82
Citronellol	**11**	81	91
Benyzl alcohol	**12**	82	ND

[a] Yields reported are based on purified product. [b]Irradiation performed on a 0.01 M solution. [c]Lower isolated yields were due to the volatility of the starting alcohol.

Deprotection: The sisyl ethers were, somewhat surprisingly, also stable towards selected fluoride reagents. Three such reagents were examined; KF + 18-crown-6, cesium fluoride and tetrabutylammonium fluoride. The sisyl ether proved to be stable to the former two reagents in THF. However, deprotection occurred in the presence of tetrabutylammonium fluoride. These results are summarized in Table 2.

Table 2: Products recovered from various stability tests

Organometallic Reagents			Fluoride Reagents			Other Nucleophiles	
CH_3MgBr	Ph_3PBr	Jones	KF/18-crown-6	nBu$_4$NF	CsF	$LiAlH_4$	nBuLi
100% **6b**	88% **6b**	100% **6b**	100% **6b**	100% **6a**	100%**6b**	**6a** + other products	**6a** + other products

The silyl ethers readily underwent photodegradation at 254 nm (Table 1). As the sisyl ethers were soluble in CH_2Cl_2, and because of the convenient removal of this solvent by evaporation, it was used throughout for the photolysis with wet methanol as the proton source. All irradiations were complete within 30 minutes. The deprotection proceeded rapidly to give high yields of the starting alcohol (62-95%, Scheme 1B, Table 1).

Hydrolytic Deprotection: Our original paper reported that the sisyl ether of cholesterol was stable to acidic aqueous acetone.[12] It is not very soluble in partly aqueous media and, therefore, the compounds listed in Table 3 were chosen instead for the kinetic study, although they are not entirely representative of the more complex molecules typically involved in synthetic routes. In order to determine the hydrolytic stability of the sisyl

group, relative to that of the TBS group, the rates of acid-catalyzed hydrolysis of a series of both sisyl and TBS ethers were measured. A modification of the procedure established by Corey *et al.*, which utilizes an aqueous solution of THF and acetic acid, was found to be suitable.[7] Pseudo-first-order rate constants were obtained by monitoring the loss of silyl ether by ^{1}H NMR and comparing the integration of the peaks corresponding to starting material and products. The k_{obs} values were calculated from least squares linear regression analysis of plots of the silane concentration as a function of time. The ^{1}H and ^{13}C NMR spectra were compared before and after samples were spiked with an authentic sample of the alcohol, confirming it to be the major product of hydrolysis. The observed rate constants for acidic hydrolysis of the sisyl and TBS ethers are given in Table 3.[17]

Table 3. Rate constants for acidic hydrolysis of silyl ethers ROSiR'$_3$

SiR'$_3$	R (compound no.)		
	CH_2CH_2Ph	CH_2Ph	C_5H_9
$Si(Si(CH_3)_3)_3$	3.74×10^{-2} s^{-1} **10**	1.94×10^{-2} s^{-1} **12**	1.30×10^{-2} s^{-1} **5**
$Si(CH_3)_2t$-Bu	6.04×10^{-3} s^{-1} **13**	3.53×10^{-3} s^{-1} **14**	3.49×10^{-3} s^{-1} **15**

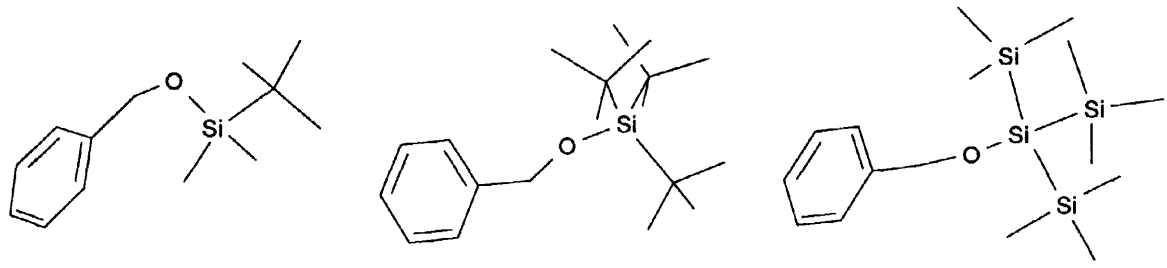
Several subtly different mechanisms for the acidic hydrolysis of silyl ethers have been proposed based on both kinetic[18] and stereochemical studies.[19] Despite evidence for the occurrence of general[20] and specific acid catalysis[21] in hydrolysis, and for the expansion of coordination at silicon in alcoholysis,[22] the specific structures involved in the rate-determining step remain elusive.

The relative rates of different reaction classes as a function of relative steric bulk have been elegantly reviewed by Hwu.[4] In general, the dominant factor in the hydrolysis rates of alkoxysilanes is steric bulk around the silicon nucleus. The decreasing rate found on going from compounds **13** to **15** and **10** > **12** > **5**, where the alcohol bulk is increasing, is consistent with this relationship.[2,10]

The 10 fold rate enhancement of hydrolysis of sisyl ethers relative to TBS ethers in aqueous acid may similarly be simply the result of a difference in steric contributions from three $SiMe_3$ groups *versus* two methyl groups and a *t*-butyl group. The proximity of the latter groups to the reacting silicon centre, as a function of the shorter Si-C than Si-Si bonds, better shields the silicon in **14** from nucleophilic attack. This effect can be seen from the volumes, calculated using the MM2 force field, of three related compounds:[23] **14**, **16** and **12** were calculated to have volumes of 389, 532 and 595 Å^3, respectively (Chart 1). All the increased volume on going from **14** to **16** results from an increased number of proximal, shielding methyl groups. One would expect the latter compound to react more slowly than **14**.[4] By contrast, the change in volume from **16** to **12** results from moving the shielding methyls away from the silicon centre. Thus, the increase in volume in this case corresponds to an increased accessibility of nucleophiles to the silicon centre. We have previously observed that the central silicon atom is more susceptible to nucleophilic attack than the external $SiMe_3$ groups in sisyl-containing molecules.[24]

This direct dependence of relative rates on steric effects seemed reasonable for acid-catalyzed hydrolysis in aqueous acid. However, the picture is not this simple. When the rates of hydrolysis of **14** and **12** were measured using *p*-toluenesulfonic acid·monohydrate in $CDCl_3$ a threefold rate enhancement of hydrolysis of **14** over **12** was observed. This reversal of relative rate clearly cannot have its origin in steric effects if the preceding arguments are correct.

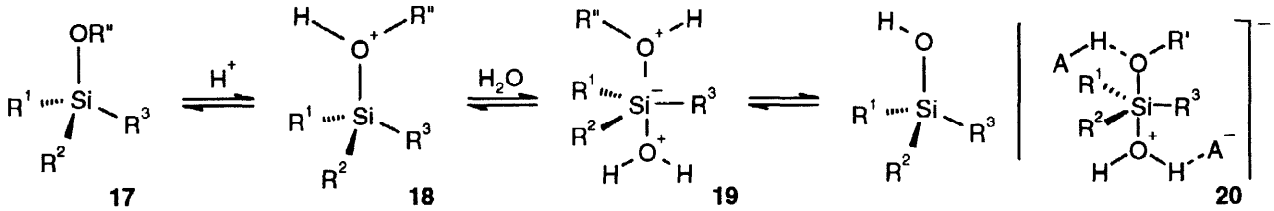
The basic steps involved in acidic hydrolysis are shown in Scheme 2. In acetic acid / water the first two steps (**17** → **18** → **19**) are likely to be rapid equilibria: there is an excess of both water and acid in the reaction. Furthermore, the reaction can be facilitated by general and specific acid and base catalysis, **20**.[20,21] By contrast, in $CDCl_3$, the concentration of acid and water are at once equal and relatively low. Thus, under these conditions the rate determining step may well be different. However, these differences in reaction conditions should affect the two different alkoxysilanes similarly. To what, then, can one ascribe the changeover in reactivity?



Volume: **14** 389 Å^3 **16** 532 Å^3 **12** 595 Å^3

Chart 1

The mechanism of acid-catalyzed hydrolysis of alkoxysilanes is affected by a variety of factors. In acidic media, electron donating groups on either silicon or the alcohol carbon accelerate the rate of hydrolysis, whereas in basic media, the rate is accelerated by electron withdrawing groups on either silicon or the alcohol carbon.[10,25,26] The reaction course is also affected when the leaving group ability is improved by the use of polar solvents and by solvents capable of hydrogen bonding to the leaving group.[10,27] For example, stereochemical studies of alkoxide/alkoxide exchange at silicon showed a dramatic crossover from retention to inversion of configuration at silicon with increasing alcoholic content in the solvent, which was attributed to two different mechanisms.[28] A further important factor in the rate is the ease of coordination expansion.[29]



Scheme 2

Silicon atoms bearing electron-withdrawing groups are better able to undergo coordination expansion.[30] As the intrinsic barrier to extracoordination will be a component of the rate of the reaction (from **18** → **19**), the relative ability of sisyl *versus* TBS groups to undergo extracoordination needs to be considered. While both alkyl groups and silyl groups are inductive electron donors, the trimethylsilyl groups on the sisyl group are more efficient donors. This can be seen from the increased shielding in the ^{29}Si NMR (Table 4). It is, therefore, conceivable that the lower hydrolysis rate of sisyl than TBS ethers in $CDCl_3$ could be a manifestation of a decreased facility for extracoordination. That is, while the steric barrier to hydrolysis of a sisyl group appears to be lower from the data shown in Table 3, which should not be affected by solvent conditions, the electronic barrier to a pentacoordinate intermediate or transition state is higher in solvents of low polarity

and/or where hydrogen bonding is unable to facilitate the reaction. Thus, the rate of hydrolytic cleavage of sisyl groups can be predictably modified by judicious choice of solvent.

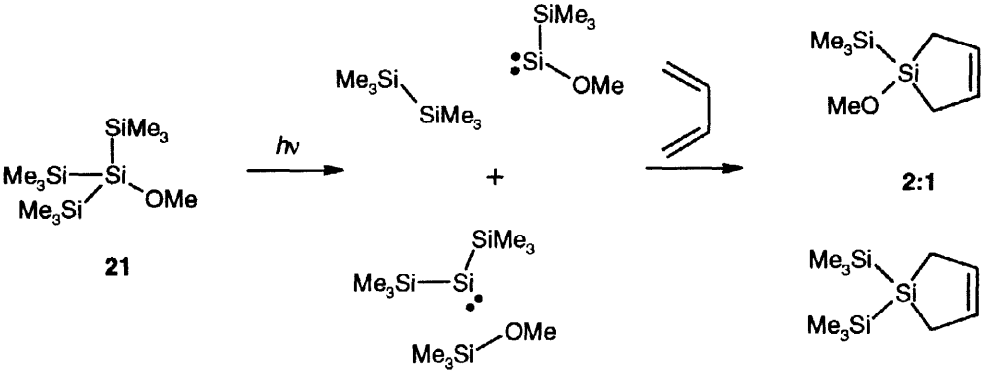
Table 4: ^{29}Si Chemical shift values (δ) of the central Si atom in ROSiR'$_3$

SiR'$_3$	R		
	CH_2CH_2Ph	CH_2Ph	C_5H_9
Si$(CH_3)_2$*t*-Bu	18.80	19.44	15.82
Si$(Si(CH_3)_3)_3$	1.47	3.47	11.30

Photodeprotection: Polysilanes are known to undergo a variety of fragmentation reactions under photolysis. Depending on the nature of the substituents[31] and the structure of the compound either the formation of radicals by bond scission,[32] or rearrangement to give carbosilanes ($R_2MeSiSiR_3 \rightarrow R_2HSiCH_2SiR_3$),[33] are known to occur. However, the more common reaction is the extrusion of silylenes,[34,35] which can in some cases subsequently lead to silenes or disilenes.[36,37]

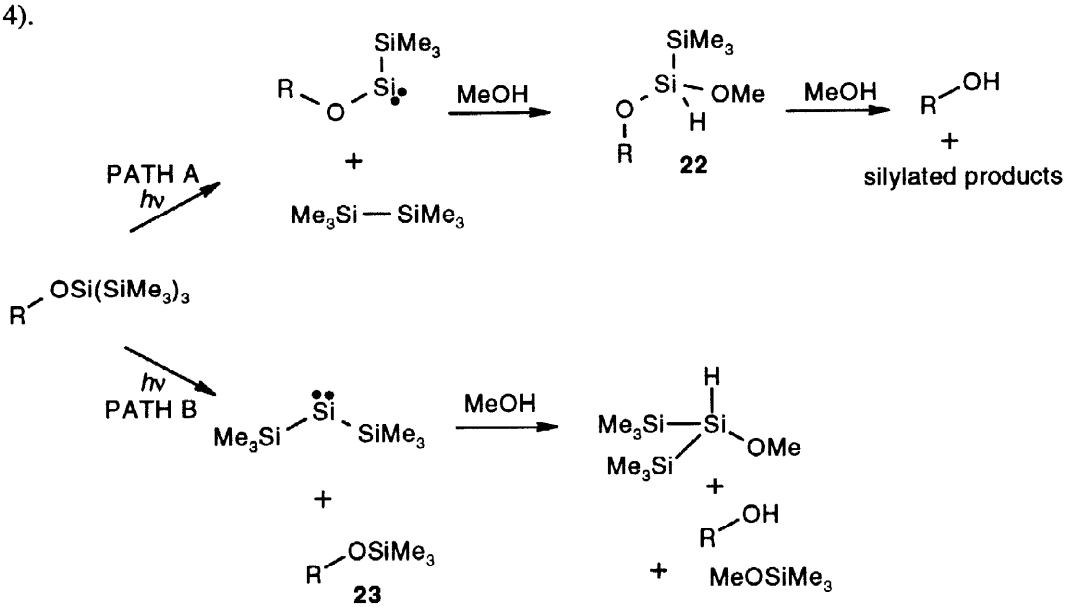
We described above the deprotection of sisyl ethers using photochemical irradiation at 254 nm in CH_2Cl_2 containing aqueous methanol. Previous work on the photolysis of alkoxypolysilanes is limited; we are unaware of the utilization of polysilanes as a protecting group methodology. The elegant work of Gaspar has shown that the sisyl ether of methanol **21** extrudes silylenes via two different regiochemical pathways, in a 2:1 ratio, as shown by trapping experiments with 1,3-butadiene (Scheme 3).[38] It seemed likely that the mechanism of deprotection of the sisyl ethers under photolysis similarly occurred via silylene formation and subsequent trapping by methanol to give **22** or extrusion of alkoxytrimethylsilanes **23** (Scheme 4).

To examine this possibility, we photolyzed sisyl ethers **12** and **5**, respectively, using 2,3-dimethyl-1,3-butadiene as a silylene trap. The reaction mixture was not amenable to NMR analysis. As we wanted to examine the product mixture prior to hydrolysis, the volatile reaction products were directly examined using GC/MS. In the case of **12**, compound **24** was the major product observed. By contrast, only compound **26** was detected by GC/MS after photolysis of 1-[tris(trimethylsilyl)siloxy]cyclopentane **5** in the presence of 2,3-dimethyl-1,3-butadiene. Presumably, the cyclic products result from trapping of bis(trimethylsilyl)silylene **25** (Scheme 5) and silylene, **27**, respectively (Scheme 6). In both experiments, only products from a single silylene could be detected.

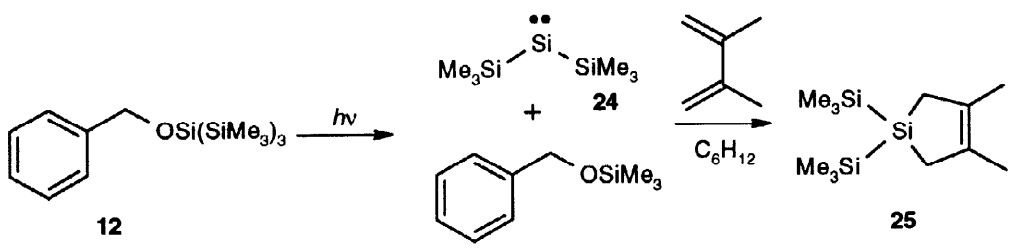


Scheme 3

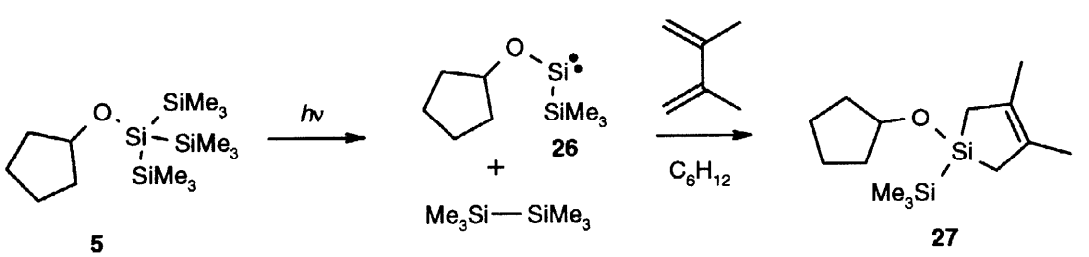
It is not clear why the benzyl derivative preferentially underwent photocleavage via Path B (Scheme 4, R = $PhCH_2$) whereas the cyclopentyl derivative followed Path A (Scheme 4, R = C_5H_9). However, these results are consistent, in the cyclopentyl case, with steric pressure in the transition state favouring $Me_3SiSiMe_3$ extrusion. Irrespective, the resulting products, silylene trapped by methanol **22** or alkoxytrimethylsilane **23**, will be more readily hydrolyzed than the respective starting materials for the steric reasons noted above (Scheme 4).



Scheme 4



Scheme 5



Scheme 6

CONCLUSION

Sisyl ethers are readily prepared from primary and secondary alcohols. These groups are stable to many of the reaction conditions normally employed in organic synthesis as is the case for silyl ethers in general. The

protective nature of the sisyl group has its origins in reasonable resistance to hydrolysis on steric grounds. Deprotection can be carried out readily by converting the sisyl ether to a hydrolytically more labile alkoxysilane via photolysis, which can then regenerate the original alcohol under mild conditions.

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EXPERIMENTAL SECTION

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer with $CDCl_3$ as an internal standard. ^{29}Si NMR spectra were recorded on a Bruker AC-300 spectrometer (at 59.6 Hz). IR spectra were recorded on a Biorad spectrometer. Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of 200 °C on a VG Instruments analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system.

Gas chromatographic (GC) analyses were carried out using a Hewlett-Packard 5890A gas chromatography equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3393A integrator, and a DB-1 megabore capillary column (30m x 0.54mm Chromatographic Specialties, Inc.). Mass spectra and GC/MS analyses were recorded on a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 fused silica capillary column (30m x 0.25mm; Chromatograph Specialties, Inc.).

The starting alcohols were obtained from Aldrich and were used without further purification after checking their purity using ^1H NMR. DMAP was purchased from Aldrich and used without further purification. CH_2Cl_2 was distilled from P_2O_5. The reagents used to test the stability of the silyl ethers were also purchased from Aldrich and used without further purification. Tris(trimethylsilyl)silyl chloride **1** was prepared using the procedure reported by Bürger *et al.*[13]

General Procedure for protection of the alcohol. To a stirring solution of the alcohol (1 mmol) and 4-dimethylaminopyridine (DMAP) (1.20 mmol) in CH_2Cl_2 was added a solution of tris(trimethylsilyl)silyl chloride (1 mmol) in CH_2Cl_2 (1 M). The solution was stirred overnight at room temperature under N_2. Water was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was removed under reduced pressure. Separation by flash chromatography gave the products in 80-90% yields.

3,7-Dimethyl-1-[tris(trimethylsilyl)silyl)]-2,6-octadien-1-ol 2b: Geraniol (161 mg, 1.00 mmol), DMAP (147 mg, 1.20 mmol), CH_2Cl_2 (1.0 mL), **1** (340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 296 mg (74%) of a clear oil **2b** was obtained. ^1H NMR ($CDCl_3$): δ 5.22 (t, J=0.8 Hz, 1H), 5.07 (t, J=0.8 Hz, 1H), 4.03 (dd, J = 0.9, 5.11 Hz, 2H), 2.01 (m, 4H), 1.65 (s, 3H), 1.56 (d, J=0.9 Hz, 6H), 0.17 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 136.3, 131.5, 125.0, 124.1, 65.1, 39.5, 26.4, 25.7, 17.7, 16.5, 0.3; ^{29}Si NMR ($CDCl_3$): δ 2.75, -

16.04; IR (neat, KBr): ν 2958, 2896, 1443, 1380, 1250, 1061, 840, 756 cm^{-1}; MS (EI, m/z): 263 $(Si(TMS)_3^+$, 48); UV (hexane) λ_{max} = 196 nm, ε_{254} = 1007.

1-[Tris(trimethylsilyl)silyl]decanol 3b: Decanol (158 mg, 1.00 mmol), DMAP (147 mg), CH_2Cl_2 (1.0 mL), **1** (340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 344 mg (85%) of a clear colorless oil **3b** was obtained. ^1H NMR ($CDCl_3$): δ 3.45 (t, J=6.6 Hz, 2H), 1.26 (m, 16H), 0.78 (t, J=13.3 Hz, 3H), 0.18 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 68.1, 33.2, 32.0, 29.8, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2, 0.4; ^{29}Si NMR ($CDCl_3$): δ 6.88, -16.21; IR (neat, KBr): ν 2955, 2927, 2856, 1465, 1380, 1246, 1087, 837.9 cm^{-1}; MS (EI, m/z): 415 (M^++1, 8), 389 (M^+-CH_3, 31), 263 (70), 73 (100); MS (CI, NH_3, m/z): 405 (M^++1, 55), 264 $(Si(TMS)_3^+$ + NH_3, 62), 156 $(CH_3(CH_2)_9^+$, 100); UV (hexane) λ_{max} = 199 nm, ε_{254} = 1242.

2-[Tris(trimethylsilyl)silyl]octanol 4b: 2-Octanol (130 mg, 1.00 mmol), DMAP (147 mg, 1.00 mmol), CH_2Cl_2 (1.0 mL), **1** (340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 294 mg (78%) of a colorless oil **4b** was obtained. ^1H NMR ($CDCl_3$): δ 3.44 (m, 1H), 1.25 (m, 10H), 1.04 (d, J=6.0 Hz, 3H), 0.86 (t, J=7.9 Hz, 3H); 0.17 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 73.1, 39.8, 32.0, 29.6, 25.6, 23.2, 22.7, 14.1, 0.5; ^{29}Si NMR ($CDCl_3$): δ -2.90, -16.33; IR (neat, KBr): ν 2955, 2932, 2896, 1460, 1245, 1130, 1070, 1044, 836.3 cm^{-1}; MS (CI, NH_3, m/z): 303 (M^+-TMS, 2), 263 (M^+-$OSi(TMS)_3$, 100); MS (CI, NH_3, m/z) 377 (M^++1, 100); UV (hexane) λ_{max} = 199 nm, ε_{254} = 1825.

1-[Tris(trimethylsilyl)silyl]cyclopentanol 5b: Cyclopentanol (0.12 mL, 1.3 mmol), DMAP (0.18 g, 1.6 mmol), CH_2Cl_2 (2.0 mL), **1** (0.38 g, 1.3 mmol). Purification by chromatography with eluent pentane yielded 0.33 g, 90% of a clear oil **5b**. ^1H NMR ($CDCl_3$) δ 3.90 (m, 1H), 1.64 (m, 2H), 1.58 (m, 2H), 1.08 (m, 4H), 0.16 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 78.9, 35.8, 36.0, 23.4, 23.3; ^{29}Si NMR ($CDCl_3$): δ -2.72, 11.30; IR (neat, KBr): ν 2952, 2895, 1439, 1246, 1060, 836 cm^{-1}; UV (hexane) λ_{max} = 196 nm, ε_{254} = 1425; MS (EI, m/z): 263 (20), 191 (20), 175 (30), 131 (35), 73 (100); MS (CI, NH_3, m/z): 264 $(Si(TMS)_3^+$ + NH_3, 8).

1-[Tris(trimethylsilyl)silyl]cholesterol 6b: Cholesterol (387 mg, 1.00 mmol), DMAP (147 mg, 1.00 mmol), CH_2Cl_2 (1.0 mL), **1** (340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 499 mg (79%) of a white waxy solid **6b** was obtained. ^1H NMR ($CDCl_3$): δ 3.11 (m, 1H), 2.15 (d, J=7.1 Hz, 2H), 1.98 (m, 2H), 1.82 (m, 2H), 1.20-1.60 (m, 11H), 1.00-1.20 (m, 11H), 0.96 (s, 3H), 0.91 (s, 3H), 0.84(d, J= 6.6 Hz, 6H), 0.66 (s, 3H), 0.16 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 141, 121, 56.7, 56.1, 50.0, 42.6, 42.2, 39.7, 39.4, 37.5, 36.5, 36.1, 35.7, 31.8, 31.7, 28.2, 27.9, 24.2, 23.8, 22.7, 22.5, 21.0, 19.3, 18.6, 11.8, 0.3; ^{29}Si NMR ($CDCl_3$): δ -1.91, -16.36; IR (neat): ν 2948, 2852, 1458, 1245, 1074 cm^{-1}; MS (EI; m/z): 499 (M^+-1, 18), 369 (M^+-$OSi(TMS)_3$, 100); UV (hexane) λ_{max} = 198 nm, ε_{254} = 1139.

1-[Tris(trimethylsilyl)silyl]-2,2,2-trifluoroethanol 7b: 2,2,2-Trifluoroethanol (100 mg, 1.00 mmol), DMAP (147 mg, 1.00 mmol), CH_2Cl_2 (1.0 mL), **1** (2340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 335 mg (97%) of a clear colorless oil **7b** was obtained. ^1H NMR ($CDCl_3$): δ 3.74 (q, J=8.6 Hz, 2H), 0.19 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 66.0, 65.3, 0.0; ^{29}Si NMR ($CDCl_3$): δ 11.32, -15.55; IR (neat, KBr): ν 2953, 2896, 1247, 1158, 837.0 cm^{-1}; MS (CI, NH_3, m/z): 264 $(Si(TMS)_3^+$ + NH_3, 20), 90 $(Me_3Si^+$+NH_3, 100); UV (hexane) λ_{max} = 197 nm, ε_{254} = 2948.

1-[Tris(trimethylsilyl)silyl]-2-chloroethanol 8b: 2-Chloroethanol (81 mg, 1.00 mmol), DMAP (147 mg, 1.00 mmol), CH_2Cl_2 (1.0 mL), **1** (340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 292 mg (89%) of a clear oil **8b** was obtained. ^1H NMR ($CDCl_3$): δ 4.90 (t, J=6.0 Hz, 2H), 4.69 (t, J=6.1 Hz, 2H); 1.42 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 68.0, 44.9, 0.3; ^{29}Si NMR ($CDCl_3$): δ 5.55, -15.80; IR (neat, KBr): ν 2952, 2894, 1246, 1112, 836.9 cm^{-1}; MS (EI, m/z): 327 (M^++1, 64), 264 $(Si(TMS)_3^+$+NH_3, 10); UV (hexane) λ_{max} = 193 nm, ε_{254} = 1687.

1-[Tris(trimethylsilyl)silyl]-2,2,2-trichloroethanol 9b: 2,2,2-Trichloroethanol (149 mg, 1.00 mmol), DMAP (147 mg, 1.00 mmol), CH_2Cl_2 (1.0 mL), **1** (2340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 329 mg (83%) of a clear oil **9b** was obtained. ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 2H), 0.22 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 99.0, 80.1, 0.2; ^{29}Si NMR ($CDCl_3$): δ 7.13, -16.60; IR (neat, KBr): ν 2952, 2895, 1246, 1135, 836.2 cm^{-1}; MS (CI, NH_3, m/z): 264 ($Si(TMS)_3^+$+NH_3, 54), 90 (Me_3Si^++NH_3, 100); UV (hexane) λ_{max} = 197 nm, ε_{254} = 1057.

1-[Tris(trimethylsilyl)silyl]-2-phenylethanol 10b: 2-Phenyethanol (0.24 mL, 2.1 mmol), DMAP (0.29 g, 2.5 mmol), CH_2Cl_2 (3.0 mL), **1** (0.61 g, 2.1 mmol). Purification by chromatography with eluent pentane:diethyl ether = 9:1 yielded 0.50 g, 80% of a clear oil **10b**. ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 5H), 3.74 (t, J=6.9 Hz, 2H), 2.85 (t, J=6.9 Hz, 2H), 0.24 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 139.0, 129.0, 128.0, 126.0, 69.0, 39.8, 0.3; ^{29}Si NMR ($CDCl_3$): δ 1.47, -16.55; IR (neat, KBr): ν 3029, 2950, 2893, 1396, 1376, 1245, 1088, 1078, 836.9 cm^{-1}; UV (hexane) λ_{max} = 194 nm, ε_{254} = 1207; MS (EI, m/z): 263 (15), 175 (10), 131 (15), 105 (100), 73 (60); MS (CI, NH_3, m/z): 369 (100), 263 (50), 138 (50), 122 (60), 105 (70), 90 (50).

3,7-Dimethyl-1-[tris(trimethylsilyl)silyl)]-6-octen-1-ol, 11b: β-Citronellol (156 mg, 1.00 mmol), DMAP (147 mg, 1.20 mmol), CH_2Cl_2 (1.0 mL), **1** (340 mg, 1.20 mmol) in CH_2Cl_2 (1.0 mL). After chromatography, 326 mg (81%) of a clear oil **11b** was obtained. ^{1}H NMR ($CDCl_3$): δ 5.07 (dt, J=11.5, 2.68 Hz, 1H), 3.50 (t, J=13.3, 2H), 1.95 (m, 1H), 1.66 (s, 3H), 1.58 (s, 3H), 1.50-1.65 (m, 1H), 1.25-1.45 (m, 1H), 0.87 (d, J=13.0, 3H), 0.23 (s, 27H); ^{13}C NMR ($CDCl_3$): δ 130.9, 125.0, 66.4, 40.2, 37.4, 29.4, 25.8, 25.6, 19.6, 17.7, 0.4; ^{29}Si NMR ($CDCl_3$): δ 0.67, -16.2; IR (neat, KBr): ν 2955, 2896, 2857, 1450, 1379, 1246, 1076, 840.0 cm^{-1}; MS (CI, NH_3, m/z): 419 (M^+ + NH_3, 37), 264 ($Si(TMS)_3^+$+NH_3, 100%); UV (hexane) λ_{max} = 196 nm, ε_{254} = 1521.

1-[Tris(trimethylsilyl)silyl]benzyl alcohol 12: Benzyl alcohol (0.85 mL, 8.1 mmol), DMAP (1.33 g, 10.9 mmol), CH_2Cl_2 (8.0 mL), **1** (2.29 g, 8.1 mmol). Purification by chromatography with eluent petroleum ether:diethyl ether = 39:1 yielded 2.33 g, 82% of a clear oil. ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 5H), 4.59 (s, 2H), .18 (s, 27H); ^{13}C NMR ($CDCl_3$,): δ 141.7, 128.1, 126.8, 125.6, 69.3, -0.1; ^{29}Si NMR ($CDCl_3$,) δ (ppm): 3.47, -15.61; IR (neat, cm^{-1}): 2952, 2893, 2857, 1245, 1085, 1063, 836, 690; UV (hexane) λ_{max} = 193 nm, ε_{254} = 1263; MS (EI, m/z): 339 (10), 263 (90), 248 (15), 189 (30), 175 (40), 131 (25), 117 (25), 91 (100), 73 (75); MS (CI, NH_3, m/z): 372 (15), 355 (100), 264 (70), 108 (20), 90 (25); HRMS (m/z): calcd for $C_{15}H_{31}O_1Si_1$ (M^+ - CH_3): 339.1451, found: 339.0750.

1-(*t*-Butyldimethylsilyl)-2-phenylethanol 13: 2-Phenylethanol (1.5 mL, 12.5 mmol), DMAP (1.84 g, 15.0 mmol), CH_2Cl_2 (13.0 mL), *t*-butylchlorodimethylsilane (1.88 g, 12.5 mmol). Purification by chromatography with eluent pentane:diethyl ether = 19:1 yielded 2.6 g, 88% of a clear oil. ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 5H), 3.78 (t, J=7.1 Hz, 2H), 2.80 (t, J=7.1 Hz, 2H), 0.85 (s, 9H), -0.03 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 139.2, 129.2, 128.20, 126.1, 64.6, 39.7, 25.9, 18.3, -5.4; ^{29}Si NMR ($CDCl_3$) δ(ppm): 18.80; IR (neat, cm^{-1}): 3023, 2953, 2930, 2854, 1474, 1254, 1102, 827, 781, 692; MS (EI, m/z): 221 (10), 179 (100), 161 (25), 105 (50), 75 (25); MS (CI, NH_3, m/z): 254 (35), 237 (100), 196 (35), 179 (15), 122 (15), 105 (15); HRMS (m/z): calcd for $C_{13}H_{21}O_1Si_1$ (M^+ - CH_3): 221.1361, found: 221.1361.

1-(*t*-Butyldimethylsilyl)benzyl alcohol 14: Benzyl alcohol (2 ml, 19.3 mmol), imidazole (1.57 g, 23.1 mmol), DMF (20.0 mL), *t*-butylchlorodimethylsilane (2.9 g, 19.3 mmol). Purification by chromatography with eluent petroleum ether:diethyl ether = 39:1 yielded 3.69 g, 86% of a clear oil. ^{1}H NMR ($CDCl_3$): δ.29 (m, 5H), 4.73 (s, 2H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 141.4, 128.2, 126.8, 126.0, 64.9, 25.9, 18.4, -5.3; ^{29}Si NMR ($CDCl_3$) δ (ppm): 19.44; IR (neat, cm^{-1}): 2955, 2930, 2857, 1470, 1254, 1096, 1070, 838, 776, 728; MS

(EI, m/z): 165 (100), 135 (40), 91 (45); MS (CI, NH_3, m/z): 240 (75), 223 (15), 182 (15), 108 (100), 91 (20); HRMS (m/z): calcd for $C_{13}H_{22}Si_1O_1$ (M^+): 222.1439, found: 222.1429.

1-(*t*-Butyldimethylsilyl)cyclopentanol 15: Cyclopentanol (1.6 mL, 17.6 mmol), DMAP (2.58 g, 21.1 mmol), CH_2Cl_2 (18.0 mL), *t*-butylchlorodimethylsilane (2.65 g, 17.6 mmol). Purification by chromatography with eluent pentane yielded 2.61 g, 75% of a clear oil. ^1H NMR ($CDCl_3$) δ (ppm): 4.20 (m, 1H), 1.66 (m, 4H), 1.47 (m, 4H), 0.85 (s, 9H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 74.4, 35.7, 25.9, 23.1, 18.2, -4.7; ^{29}Si NMR ($CDCl_3$) δ (ppm): 15.82; IR (neat, cm^{-1}): 2951, 2930, 2855, 1468, 1252, 1060, 832, 775; MS (EI, m/z): 185 (5), 143 (50), 75 (100), 59 (10), 43 (15); MS (CI, NH_3, m/z): 201 (100), 162 (20), 133 (35), 92 (55), 74 (15); HRMS (m/z): calcd for $C_{10}H_{21}O_1Si_1$ ($M^+ - CH_3$): 185.1361, found: 185.1361.

Stability Tests

The sisyl ether, **6b**, was subjected to the conditions listed below. The progress of the reaction was monitored by TLC. After a set time (see procedures) the organic layer was separated, dried over anhydrous sodium sulfate and removed under reduced pressure. The crude product was shown by ^1H NMR to be unmodified starting material.

Treatment with Organometallic Reagents: A) To a solution of **6b** (50 mg, 0.08 mmol) in distilled THF (5.0 mL) at -78 °C was added 3.0 M MeMgBr (0.04 mL, 0.12 mmol). The solution was warmed to room temperature and acetone (5.0 mL) was added, forming the alkoxide. The reaction was quenched by the addition of H_2O (2.5 mL), the organic phase separated, dried and evaporated to give recovered 6b in 100% yield (50 mg).

B) To a solution of triphenylphosphonium bromide (57 mg, 0.16 mmol) in THF (5.0 mL) at 0 °C was added 1.6 M *n*-BuLi (0.10 mL, 0.16 mmol). The mixture was stirred for 0.5 h and **6b** (50 mg, 0.08 mmol) in THF (1.0 mL) was added. The solution was warmed to room temperature and stirring continued for 4 h. The reaction was quenched by the addition of H_2O (2.5 mL), the organic phase separated, dried and evaporated to give recovered **6b** (50 mg, 88%).

Oxidation: Compound **6b** (50 mg, 0.08 mmol) in acetone (5.0 mL) was cooled to 0 °C and a solution of Jones reagent was added maintaining the reaction temperature below 15 °C. Once the addition was complete, stirring continued at room temperature for four h. The organic phase was separated, dried and evaporated to yield 50 mg (100%) of **6b**.

Deprotection

Fluorination reactions: The fluoride source was dissolved in a solvent to which **6b** was added. The mixture was stirred, the organic phase was separated, dried and evaporated.

A) **6b** (50 mg, 0.08 mmol) in benzene (0.5 mL); 18-Crown-6 (21 mg, 0.08 mmol); benzene (2.0 mL); oven-dried KF (10 mg, 0.16 mmol); 0.5 h; stirred overnight at room temperature. Quantitative recovery of **6b**.

B) **6b** (50 mg, 0.08 mmol); TBAF (42 mg, 0.16 mmol); THF (5.0 mL) at 0 °C; then warmed to room temperature and stirred for 5 h; 6a, was recovered in a 100% yield (32 mg).

C) **6b** (50 mg, 0.08 mmol); CsF (27 mg, 0.16 mmol); THF (5.0 mL); room temperature overnight; Quantitative recovery of **6b**.

Reduction: To a solution of **6b** (50 mg, 0.08 mmol) in anhydrous diethyl ether (4.0 mL) at 0 °C was added $LiAlH_4$ (4.6 mg, 0.12 mmol). The reaction continued to stir at 0 °C for 2.5 h and was quenched by the addition of H_2O (2.0 mL). A mixture of products, including the unprotected alcohol, **6a** was obtained.
Organic Base: To a solution of **6b** (50 mg, 0.08 mmol) in THF (2.0 mL) at -78 °C was added 2.0 M *n*-BuLi (0.06 mL, 0.12 mmol). The reaction was stirred for one h at room temperature and quenched with H_2O (1.0 mL). A mixture of products, including the unprotected alcohol, **6a** was obtained.

General Procedure - Deprotection by Photolysis

A 0.1 M solution of the protected alcohol in methylene chloride with methanol was irradiated at 254 nm in a quartz cell for 30 min. and monitored by TLC until the reaction was complete. The solvent was removed under reduced pressure and the alcohol purified by flash chromatography.
2b: 3,7-Dimethyl-1-[tris(trimethylsilyl)silyl]-2,6-octadien-1-ol (52 mg, 0.13 mmol), MeOH (5 mL, 0.183 mmol), CH_2Cl_2 (1.3 mL); yield 18 mg (90%) of **2a**.
3b: 1-[Tris(trimethylsilyl)silyl]decanol (54 mg, 0.13 mmol), MeOH (5 mL, 0.13 mmol), CH_2Cl_2 (1.3 mL); yield 14 mg (68%) **3a**.
4b: 2-[Tris(trimethylsilyl)silyl]-2-octanol (50 mg, 0.13 mmol), MeOH (5 mL, 0.13 mmol), CH_2Cl_2 (1.3 mL), yield 16 mg (95%) of **4a**.
5b: 1-[Tris(trimethylsilyl)silyl]cyclopentanol (70 mg, 0.21 mmol), MeOH (9 mL, 0.21 mmol), CH_2Cl_2 (2.1 mL), yield 16 mg (88%) of **5a**.
6b: Tris(trimethylsilyl)silylcholesterol (50 mg, 0.08 mmol), MeOH (3 mL, 0.08 mmol), CH_2Cl_2 (8.0 mL), yield 27 mg (87%) of **6a**.
7b: 1-[Tris(trimethylsilyl)silyl]-2,2,2-trifluoroethanol (54 mg, 0.16 mmol), MeOH (6 mL, 0.16 mmol), CH_2Cl_2 (1.6 mL), yield 10 mg (62%) of **7a**.
8b: 1-[Tris(trimethylsilyl)silyl]-2-chloroethanol (60 mg, 0.18 mmol), MeOH (7 mL, 01.8 mmol), CH_2Cl_2 (1.8 mL), yield 13 mg (90%) of **8a**.
9b: 1-[Tris(trimethylsilyl)silyl]-2,2,2-trichloroethanol (60 mg, 0.15 mmol), MeOH (6 mL, 0.15 mmol), CH_2Cl_2 (1.5 mL), yield 20 mg (89%) of **9a**.
10b: 1-[Tris(trimethylsilyl)silyl]-2-phenylethanol (50 mg, 0.14 mmol), MeOH (6 mL, 0.14 mmol), CH_2Cl_2 (1.4 mL), yield 14 mg (82%) of **10a**.
11b: 3,7-Dimethyl-1-[tris(trimethylsilyl)silyl]-6-octen-1-ol (50 mg, 0.12 mmol), MeOH (5 mL, 0.12 mmol), CH_2Cl_2 (1.2 mL), yield 17 mg (91%) of **11a**.

General Procedure for acidic hydroylsis

In aqueous media: To an NMR tube containing the silyl ether (0.076 mmol) under N_2 at 25 °C was added THF d_8 (0.26 mL), D_2O (0.12 mL), and CD_3CO_2D (0.38 mL), to make a 0.1M solution of silyl ether. The ^1H NMR spectra were acquired initially within 2 minutes of addition of CD_3CO_2D, and subsequently every 10 minutes.
In organic media: To the silyl ether (0.07 mmol) in $CDCl_3$ (3 mL), was added *p*-toluenesulfonic acid monohydrate (0.28 mmol). The reaction was monitored by ^1H NMR every 10 minutes.

Silylene Trapping Experiments

A mixture of protected alcohol (1 mmol) and 2,3-dimethyl-1,3-butadiene (10 mmol) in hexane (10 mL) was placed in a quartz photolysis tube. N_2 gas was bubbled through the mixture for 10 minutes before irradiation. The mixture was irradiated for an hour with an array of low-pressure mercury lamps (5-9 lamps) in a Rayonet photochemical reactor at 254 nm. The progress of the reaction was monitored by GC/MS.

The photolysis of **12**, to 95% conversion, in the presence of 2,3-dimethyl-1,3-butadiene led to two major and two minor products. The major products were identified by their mass spectral data: benzyloxytrimethylsilane (23%, % refers to GC area%) (m/z) 180 (4), 165 (81), 135 (55), 91 (100), 73 (13); and **25** (33%) (m/z): 256 (M^+, 24), 183 (M^+-TMS, 55), 167 (20), 155 (20), 141 (22), 123 (27), 109 (21), 73 (100).

The photolysis of **5** in the presence of 2,3-dimethyl-1,3-butadiene to *ca.* 28% conversion led only to the formation of two major products, $Me_3SiSiMe_3$ (20%) and **27** (68%), and one unidentified minor product. The identity of $Me_3SiSiMe_3$ was shown by comparison with an authentic sample and **27** by its mass spectral data: (m/z): 268 (M^+, 3), 199 (72), 171 (30), 157 (82), 117 (100), 109 (15), 73 (93).

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