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Organophotocatalyzed C–Si Bond Fragmentation Using Silyl Ethers as Radical Precursors

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Abstract: In this work, silyl ethers of phenols and alcohols have been successfully prepared and tested as neutral carbon (silicon) centered radical precursors. The organophotocatalyzed oxidation (by the Fukuzumi catalyst) of these ethers caused the cleavage of a C–Si (or a Si–Si) bond for the release of the desired radical to be used for the forging of C(sp^3) –C(sp^3) (or C(sp^3) –Si) bonds via a Giese reaction.

Keywords: Photocatalysis; Radicals; Silyl ethers; Visible light

Introduction

Photochemical generation of carbon-centered radicals is currently a hot topic as it enables the forging of C–X bonds in a sustainable manner compared to traditional methodologies, typically employing stoichiometric amounts of reductants or oxidants, toxic species, and harsh conditions.[1] Organosilicon compounds have found application in the (photo)generation of reactive intermediates[2] also thanks to their lower toxicity compared to organostannanes.[1g,3] In this context, photogenerated silyl radicals are important in XAT reactions,[4] benzoyldiisopropylchlorosilanes were purposely designed as photocleavable protecting groups for alcohols[5] or silanols were used to generate alkyl radicals via β-scission of a LMCT complex by using Ce^{III} salts.[6] However, one of the main advantages of having a silicon atom in organic derivatives is the profound effect it exerts on their electrochemical behaviour when they contain π-systems and/or heteroatoms.[7] Thus, in compounds having heteroatoms such as oxygen, nitrogen, and sulfur, the presence of a silyl group makes them significantly easier to be oxidized. This is apparent from the E_{OX} values of ethers (e.g. **I**) and (protected) amines (e.g. **II**) in comparison with the corresponding α-silyl ethers (**Ia**) or (protected) α-silylamines (**IIa**, see Figure 1a).[7] This has important implications in photoredox catalysis since easily oxidizable silanes were used for the release of carbon radicals. The silyl moiety functions as a redox auxiliary group and is able to promote the formation of the corresponding radical cation which subsequently fragments, releasing the radical of interest.[8] Typical cases are the release of α-oxy radicals (from α-silyl ethers **Ia**[9]), α-amino radicals (from α-silylamines **III**[10]), allyl radicals (from allyl silanes **IV**[11]), benzyl radicals (from benzyl silanes **V**[12]) and acyl radicals (from acyl silanes **VI**,[13] Figure 1b). On the contrary, the reactivity of unfunctionalized tetraalkylsilanes **VII** towards monoelectronic oxidation is very low, since the oxidation potential of such compounds is >2.5 V[7c,14] thus forcing harsh conditions.

Nevertheless, it was described in the early 90s detailing the photochemical alkylation of pyrylium salts[15] and of aromatic nitriles (e.g. 1,2,4,5 tetracyanobenzene, TCB)[16] via photoinduced electron transfer with tetralkylsilanes.

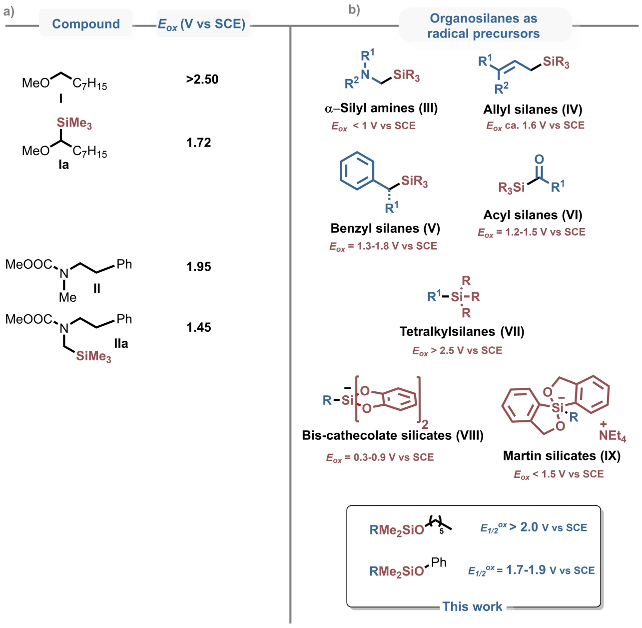


Figure 1. a) Comparison of the oxidation potential of organic compounds with those incorporating a trialkylsilyl groups. b) Silicon based derivatives used in photoredox catalysis and in this work.

In this case, the high reduction potential in the excited state of these aromatics allowed for the oxidation of R_4Si and the radical released from the resulting radical cation is then able to couple with the aromatic radical anion. Despite this was an interesting case of aromatic carbon-carbon ipso-substitution reaction,[17] the only fate of the radical is the functionalization of the absorbing species. A recent and elegant strategy for the generation of alkyl radicals makes use of hypervalent bis-catecholato silicates **VIII** (E_{OX} < 1 V vs SCE[1c,18] Figure 1b) including Martin silicates **IX** (E_{OX} ca. 1.5 V vs SCE[19]). However, the preparation of these charged silicon derivatives is not so trivial.

On the other hand, despite alcohols are very difficult to oxidize (e.g. E_{OX} EtOH > 3.5 V vs SCE[20]) their conversion into silyl ethers was found to be beneficial (the E_{OX} $EtOSiMe_3$ was reported to be lower with respect to the corresponding alcohol; > 2.5 V vs SCE[21]). The oxidative capability of the silyl ether depends on the alcohol and not on the silyl groups (as an example the E_{OX} $Et_3Si–H$ and $Bu_3Si–H$ are 2.15 V vs SCE[22] and ca. 2.5 V vs SCE,[23] respectively).

In the frame of finding new neutral radical precursors,[24] we deemed then worthwhile to investigate a more accessible class of silyl derivatives namely silyl ethers as alkyl radical precursors.

Whereas the (direct) photochemistry of such compounds has received only few attentions,[25–27] sparse examples were reported on the photocatalyzed generation of alkyl radicals from silyl ethers by using cyanoarenes as photooxidants. Thus, irradiation of TCB (320 nm), in the presence of *tert*-butyldimethyl(octyloxy)silane led to the release of a *tert*-butyl radical that coupled with the generated radical anion of the cyanoarene to afford *tert*-butylated tricyano benzene as the exclusive product.[28] However, when an electron-poor olefin was present in the mixture, Giese-type reaction competes with the functionalization of the cyanoarene, resulting in a hydroalkylation reaction.[29]

In view of these premises, we thus reconsidered the potential of silyl ethers as precursors of C and Si radicals under photoredox catalyzed conditions, by taking advantage on the oxidizability of the Si–O bond in trialkylalkoxysilanes.

Results and Discussion

Two different families of silyl ethers were synthesized, namely phenyl silyl ethers **1 a-1 g** and alkyl silyl ethers **1 h-1 o** (Chart 1). These compounds were easily prepared in excellent to quantitative yields starting from phenols or alcohols by treatment with the corresponding trialkyl silyl chlorides in the presence of DBU (for further details see the Supporting Information, Figures S1 and S2).

We thus measured the oxidation potential of the silyl ethers obtained to have indication on the choice of the photocatalyst to be used (Figures S3–S5). As apparent from Table 1, compounds **1 a-g**, derived from phenols, are markedly easier to be oxidized with respect to that formed from alcohols. The aromatic silyl ethers have an $E^{1/2}_{OX}$ of about 1.7–1.9 V vs SCE whereas the aliphatic ones have $E^{1/2}_{OX}$ values up to 2.4 V vs SCE except the case of disilane **1 o** ($E^{1/2}_{OX}$ = 1.55 V vs SCE).

To confirm our hypothesis, we focused on the *tert*-butylation of phenyl vinyl sulfone by **1 a** to form compound **3** as the model reaction. We embarked on a deep optimization process by screening different solvents and solvent mixtures, different photocatalysts

Table 1. Oxidation potential of the silyl ethers tested in the present work.

Compound	$E^{1/2}_{OX}$ ($R^{\bullet +}/R$) V vs SCE	Compound	$E^{1/2}_{OX}$ ($R^{\bullet +}/R$) V vs SCE
1 a	+1.84	**1 h**	+2.03
1 b	+1.70	**1 i**	+2.27
1 c	+1.68	**1 j**	+2.32
1 d	+1.68	**1 k**	+2.44
1 e	+1.94	**1 l**	+1.95
1 f	+1.69	**1 m**	+2.45
1 g	+1.82	**1 n**	+2.05
Biphenyl	+1.95	**1 o**	+1.55

(including photoorganocatalysts Acr$^+$-Mes and NMQ$^+$ salts) under different conditions.

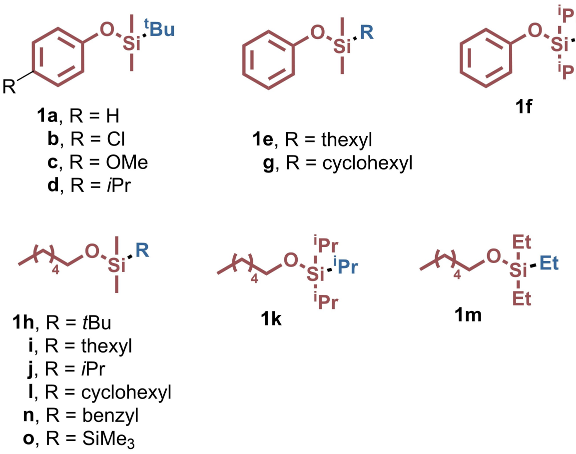
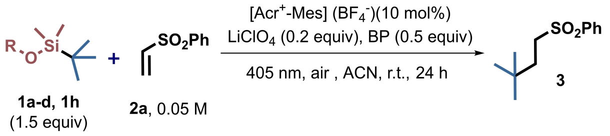


Chart 1. Silyl ethers tested in the present work.

A selection of the obtained results is shown in Table 2 (see Tables S2 and S3 for further details). The best conditions involved the use of Fukuzumi's catalyst, (9-mesityl-10-methylacridinium tetrafluoroborate, 10 mol%) having an E_{RED}(*PC^n/PC^{n-1}) = + 2.06 V vs SCE.[30] As previously observed in the oxidation of silanes,[12b] a lithium salt ($LiClO_4$, 0.2 equiv.) and biphenyl (BP, 0.5 equiv.) as additives were beneficial for the reaction. Upon irradiation of the resulting air equilibrated acetonitrile solution containing vinyl sulfone (1 equiv.) at 405 nm (Evoluchem lamp, 18 W) for 24 h gave product **3** in 94% yield (Table 2, entry 1). The additives have a key role on the performance of the reaction because their absence caused a yield drop (entries 2–4).

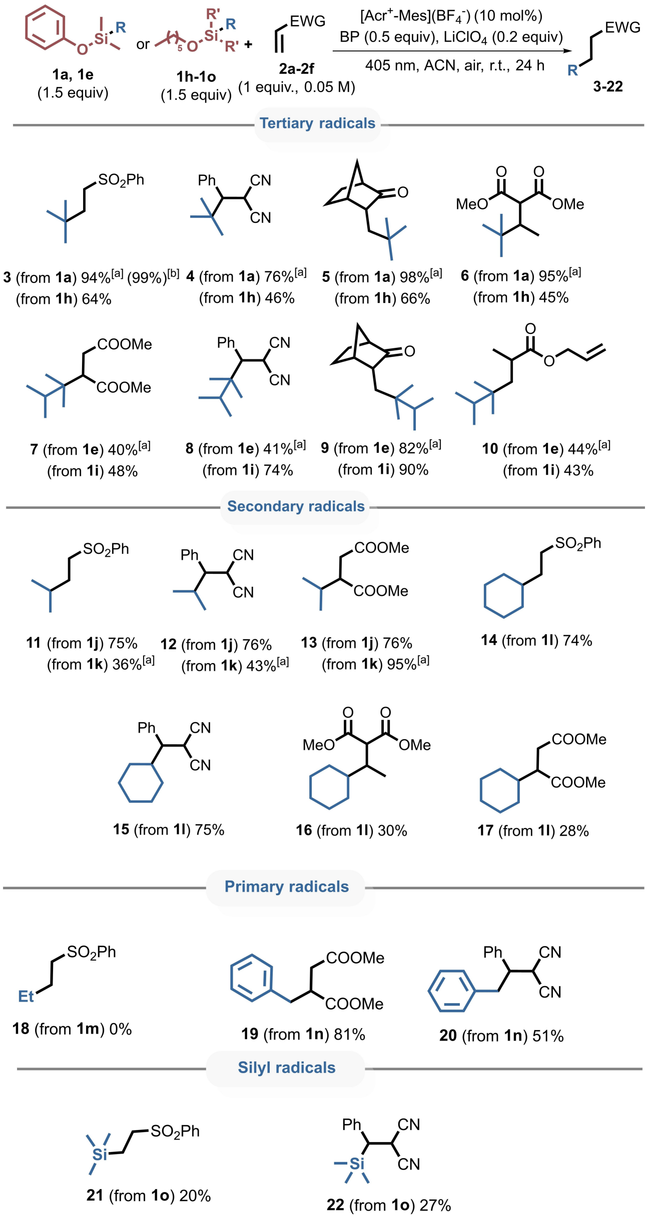
Table 2. Selected optimization results for the synthesis of **3**.



Entry	Deviation from standard conditions	**3** (%) yield
1	None	94
2	No additives, 72 h	61
3	Only $LiClO_4$ (0.2 equiv.) as additive	84
4	Only BP (0.5 equiv.) as additive	59
5	[Acr$^+$-Mes](BF_4^-) (5 mol%)	67
6	**1 a** (1 equiv.)	63
7	ACN/H_2O (9:1), No additives	–
8	NMQI (10 mol%) as PC, only BP (0.5 equiv.) as additive	–
9	[Ph_3Py^+](BF_4^-) (10 mol%) as PC	–
10	**1 b** (1.5 equiv.) in place of **1 a**	71
11	**1 c** (1.5 equiv.) in place of **1 a**	–
12	**1 d** (1.5 equiv.) in place of **1 a**	–
13	No light	–
14	No PC	–
15	**1 h** (1.5 equiv.) in place of **1 a**	64

Decreasing the amount of the acridinium salt to 5 mol % (entry 5) or of the silyl ether to 1 equiv. (entry 6) had a deleterious effect on the reaction yield. Addition of a protic solvent (water) to the reaction mixture was likewise detrimental to the reaction course (entry 7). When the photocatalyst was replaced by other strong oxidizing PCs such as NMQ$^+$ (E_{RED}(*PC^n/PC^{n-1}) = +2.7 V vs SCE)[31] and pyrylium salt (E_{RED}-(*PC^n/PC^{n-1}) = +2.3 V vs SCE)[32] the product was not formed (entries 8, 9). We next evaluated the effect of the substituents on the aromatic ring of the *tert*-butyl silyl ethers on the reaction outcome. Interesting, the substitution led to a better oxidizability of the silyl ethers (compare the $E^{1/2}_{OX}$ of **1 a** with **1 b-d**, Table 1). Only in the case of chloroderivative **1 b** product **3** was obtained to some extent (entry 10). No alkylation took place when the silyl ethers contained an electron-donating group such as in compounds **1 c** or **1 d** that are not significantly consumed in the reaction (entries 11, 12). The experiments performed in the absence of light (entry 13) and of the PC (entry 14) suggested a light-induced photocatalyzed process. Moreover, product **3** was likewise obtained (albeit in a lower yield, 64%) starting from aliphatic silyl ether **1 h**.

With these results in hand the scope was broadened by combining electron-poor olefins **2 a-f** (Chart S1) and different silyl ethers, as depicted in Scheme 1. At first, both aromatic and aliphatic silyl ethers successfully generated different tertiary radicals (*tert*-butyl and thexyl groups) and compounds **3–10** were obtained in moderate to excellent yields. Sulfone **3** was likewise prepared in almost quantitative yield under flow conditions allowing to double the concentration of the olefin to 0.1 M and shortening the irradiation time from 24 h to 2 h (the optimization table and the set-up used are shown in the supporting information, Table S4, Figures S7 and S8). Secondary carbon-based radicals such as *i*Pr and *c*C_6H_{11} were then obtained but only from aliphatic silyl ethers (compound **1 f** is not consumed upon irradiation). This fact gave us the opportunity to compare the performance of silyl ether **1 j** with the triisopropyl silyl ether **1 k**. The release of the secondary radical (via Si–^{i}Pr bond fragmentation) was exclusive even from **1 j** where no competitive liberation of the Me radical occurred. As a matter of fact, there is not a strict correlation between the formation yield of **11–13** (>75% in the favorable cases) and the silyl ether used. The trapping of the cyclohexyl radical generated from **11** was largely affected by the Michael acceptors employed (see the variable overall yields in the formation of compounds **14–17**). No alkylation product **18** was detected when



Scheme 1. Scope on the alkylation of Michael acceptors. Conditions: **1** (0.075 M, 1.5 equiv., 0.375 mmol), **2** (0.25 mmol), [Acr$^+$-Mes] (BF$_4^-$) (10 mol%), LiClO$_4$, (0.2 equiv.) and biphenyl (0.5 equiv.) in MeCN (5 mL), air, under 18 W LED irradiation (405 nm) at r.t. for 24 h. Isolated yields. [a]GC-yield using undecane as standard. [b]Reaction performed under flow conditions: **2a** (0.1 M), 2 h.

testing silyl ether **1m** as possible ethyl radical precursor in the reaction with **2a** (**1m** not consumed in the reaction). Nevertheless, primary benzyl radicals were photogenerated and used for the forging of a C–C bond in benzylated derivatives **19–20**.

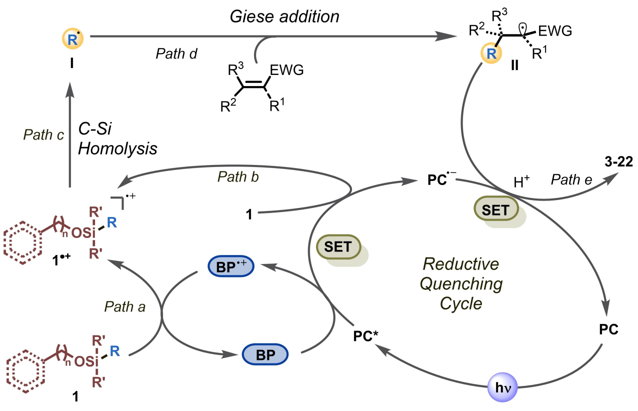
Noteworthy, compound **19** is a precursor of benzylsuccinic acid (a potent inhibitor of Carboxypeptidase A)[33] directly synthesized from commercially available materials.

Gratifyingly, silicon centered radicals were generated as well via a Si–Si bond fragmentation in the photocatalyzed oxidation of **1o** to give silanes **21** and **22** in a modest yield.

Stern–Volmer quenching data on the photocatalyst employed[34] have been collected to have insights on the reaction mechanism. As a matter of fact, the photocatalyst emission was quenched both in the presence of aromatic silyl ether **1a** (Figure S10), and BP (Figure S12) but not with aliphatic derivative **1h** (Figure S11).

The effect of BP is apparent in the synthesis of ketone **9**. The absence of BP caused a dramatical decrease on the yield (40% by GC analysis) when starting from **1e**, but no reaction occurred when using the corresponding aliphatic derivative **1i** (virtually untouched after the irradiation). Based on the results obtained we propose the mechanism summarized in Scheme 2. The photocatalyst is the only species responsible for the absorption of the visible light radiation supplied (see Figure S9). The excited photocatalyst interacted, in a first SET event, with BP to release the corresponding radical cation BP$^{\bullet+}$. The latter species then is quenched by the silyl ether **1** (path a) allowing the regeneration of BP with the concomitant formation of the radical cation $\mathbf{1}^{\bullet+}$.

Biphenyl has been previously used as secondary donor to ameliorate the performance of the SET reaction between the PC and the electron donor.[35,36] The oxidant capability of the BP$^{\bullet+}$ has been measured by CV technique ($E^{1/2}_{OX}$ BP = +1.95 V vs SCE, Table 1, Figure S6) in accordance with the literature.[37] This value is not so different from that of the excited PC. This means that the oxidation of silyl ethers **1a-1g** by BP$^{\bullet+}$ is always thermodynamically favoured, contrary to aliphatic silyl ethers **1h-1o** (except for **1o**) where $E^{1/2}_{OX}$ > 2.0 V vs SCE. Nevertheless, the difference on the $E^{1/2}_{OX}$ of aliphatic silyl ethers and the



Scheme 2. Proposed mechanism.

oxidant capability of the $BP^{\bullet+}$ is, however small, and the SET may likewise take place. BP has the role to separate the reacting species formed after the initial SET between the PC and **1**. The quenching operated by BP on the excited PC (see Figure S12) avoids the unproductive back electron transfer between PC* and the silyl ethers. The direct SET between PC* and **1** (at least for aromatic derivatives, path b) has, however, a role in the reaction. As a matter of fact, aliphatic silyl ethers (contrary to BP) poorly quenched the excited acridinium salt confirming again the requirement of the secondary donor. This fact could be explained by the different lifetime of the oxidizing species viz. ca. 6 ns for the excited acridinium salt[30] and ca. 10 μs (in acetonitrile) for the biphenyl.[38] In addition, the use of $LiClO_4$ is crucial to improve the overall yield (see entries 2–4, Table 2) since it is known to enhance the conductivity of the reaction media and to stabilize the charged species formed.[12b,36a] In analogy to tetraalkylsilanes, the radical cation $\mathbf{1}^{\bullet+}$, upon fragmentation, releases a carbon or a silicon centered radical **I**. The radical cation fragmentation leads in each case to the release of the more stable radical (e.g. tertiary, secondary, benzyl) and there is no competition of the methyl radical liberation in solution. Surprisingly, secondary radicals were generated only when using aliphatic but not aromatic silyl ethers. This fact could be justified by the higher stability of the radical cation intermediate in the latter case hampering the Si–C bond fragmentation when a less stable radical is released.

The fate of the radical cation contrasts with that observed in the monoelectronic electrochemical oxidation of trialkylsiloxybenzenes in protic media known to give quinones by a desilylation rather than a radical release.[39] The photogenerated carbon or silicon-based radicals were engaged in a Giese reaction with Michael acceptors to afford radical adducts **II** (path d). The subsequent SET event with the reduced form of the photocatalyst restarted the catalytic cycle on one hand and formed the corresponding carbanion on the other hand, that upon protonation delivered the alkylated products **3—22** (path e).

Conclusions

The strategy reported herein represents an attractive approach for the generation of carbon-based and silicon-based radicals under free-metal visible light conditions. The uncharged radical precursors are easy to synthesize in excellent to quantitative yields and in a high purity by using cheap and commercially available starting materials. Besides, silyl ethers are bench stable compounds that can be stored with no precautions. The protocol developed has been applied on the functionalization of small molecules under batch or flow conditions and the thus formed derivative can serve as building blocks for further synthetic applications. This method allowed to forge mainly $C(sp^3)–C(sp^3)$ bonds, currently a hot topic in synthetic chemistry, and extremely demanded in drug development processes by increasing the Fsp^3 (number of sp^3 hybridized carbons/total carbon count) thus enhancing the probabilities to obtain a bioactive compound.[40] The reaction described could have interesting implications in the degradation of thermally stable volatile methyl siloxanes (toxic and environmental persistent derivatives) where the cleavage of the inert Si–C bonds is mandatory for their complete degradation.[41]

Experimental Section

General Procedure for the photocatalyzed preparation of compounds 3–22. A solution of the corresponding silyl ether (**1 a-g** or **1 h-o**) (1.5 equiv. 0.075 M), the corresponding electron-poor olefin (1 equiv., 0.05 M), $[Acr^+\text{-}Mes]\ (BF_4^-)$ (10 mol %), $LiClO_4$, (0.2 equiv.) and biphenyl (0.5 equiv.) in MeCN (0.05 M) was prepared in a Pyrex glass vessel (see Figure S1) and irradiated for 24 h at 405 nm (18 W Evoluchem lamp). When using ethers **1 a-g**, the yield was determined by GC analysis (undecane as standard). When using ethers **1 h-o**, the crude mixture was concentrated in vacuo and the residue was purified by flash column chromatography (SiO_2) yielding the desired products.

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